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TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY  
PHYSICAL CHEMISTRY, METALLOGRAPHY AND KINDRED SUBJECTS

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# THE ELECTRICAL DOUBLE LAYER.

A COLLECTION OF PAPERS CONTRIBUTED TO A GENERAL DISCUSSION OF THE SOCIETY WHICH IT HAD BEEN INTENDED TO HOLD IN THE UNIVERSITY OF CAMBRIDGE IN SEPTEMBER, 1939.

## GENERAL INTRODUCTION.

By ERIC K. RIDEAL.

Some time ago a committee of the Society considered that a general survey of the electrical double layer at interfaces and on colloidal particles was now due and would give rise to valuable discussion. It was also hoped that such a discussion would serve to clarify the apparently somewhat diverse views held as to the cause of the apparent separation of charges when interfaces are formed, and their distribution when equilibrium was established. This view was emphasised by the fact that the beautiful electrophoretic method of separation introduced by Tiselius is now receiving such general application in biophysical laboratories. Again the study of the potential distribution at biological interfaces of living material has revealed, in spite of the difficulty of unravelling these highly complex systems, that the electrical measurements can at least be employed as useful criteria of the "proper" functioning of the complete chain of reactions which constitute the difference between the organised and disorganised or dead systems. The phase boundary potentials may indeed prove to be a regulating factor in some of these reactions. During the period of the activities of the committee, a discussion on lyophobic colloids held in Holland has resulted in the completion of a collection of valuable and interesting papers.

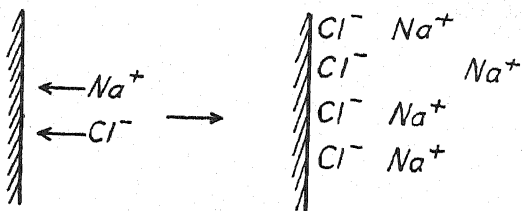
Unfortunately, owing to the outbreak of war, it has proved impossible to hold the discussion of the Faraday Society, but since many of the contributors have been kind enough to complete their manuscripts, it has occurred to the Council that these might be published together. For these papers, together with those of our Dutch colleagues, cover the more important and interesting properties associated with the electrical double layer.

Our view as to both the origin and the structure of the electrical double layer in colloidal systems is at the present time somewhat lacking in preciseness. This ambiguity is most clearly demonstrated in considering the phenomenon of electrokinetic migration of a colloidal particle in an electric field. One view which even at the present time has several protagonists may be said to have originated from Pauli's concept of the electrical structure of a colloidal particle in a solution of a dilute electrolyte. According to this view, the colloidal particle, which must be an ionogenic one, may be regarded as a large

multivalent ion, the ionogenic salt linkages present on the surface undergoing more or less complete surface dissociation in the solution. The charge on the particle which is responsible for its motion in the field is merely the result of dissociation of certain of these groups, and the maximum valency or charge is attained when all the surface groups are ionised. The consequences of this view are that all systems which exhibit electrokinetic phenomena must be ionogenic, and that the maximum charge attainable is specific for the particle or surface being merely an expression for the number of ionogenic groups constitutive in the surface of the particle.

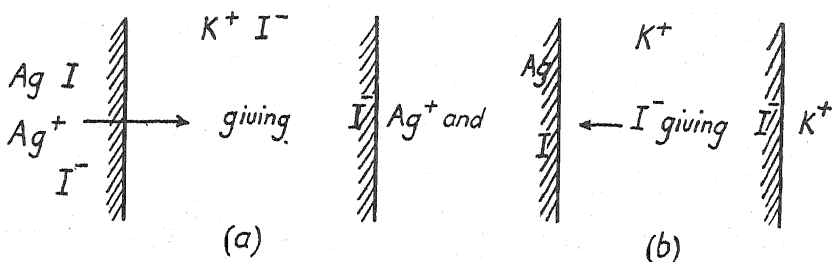
The alternative point of view is that based upon adsorption. Here we assume that at the interphase there is an electrolyte held adsorbed as ion pairs and that one kind of ion is held more firmly by the particle than the other. The ion pair thus constitutes a dipole orientated with respect to the interface. The total number of ion pairs adsorbed per square centimetre of surface can be calculated, either from the Gibbs adsorption equation or from the Lippmann equation, according to the type of interphase which is being considered. Of these adsorbed ion pairs, a certain number will be dissociated in the sense that the more loosely held ion will tend to wander off into the solution. This imparts a net charge to the surface. This charge and thus the number of ion pairs dissociating is determined either indirectly by the methods employed for calculating the  $\zeta$  potential or directly by polarisation experiments. This surface dissociation of the ion pairs is brought about by thermal agitation, and it is clear that owing to electrostatic effects the extent of such surface dissociation must be much less than that existing in the ion pair system when dispersed in a three dimensional phase. The "diffuse" ionised part of the ion pairs on the surface is the part responsible for the electrokinetic phenomena and the whole system of adsorbed ion pairs, together with the diffuse ionised portion, constitutes the Helmholtz Gouy ionic distribution.

We may note, however, that the original system of ion pairs may be created by different methods dependent on the nature of the homogeneous phases in contact with the interphase. Thus, if one phase is impermeable to ions, the layer is formed by adsorption. This may be termed Gouy or specific adsorption, and depicted as follows:—



Again, if one of the phases is a conductor and thus permeable to electrons, the ion pair system may be formed by passage of a current across the interphase.

A third process of creating a layer of ion pairs at the interphase is noted in those cases where one of the homogeneous phases is ionogenic to form ions soluble in the other phase, *i.e.* the boundary is selectively permeable to an ion; here two distinct mechanisms are operative, as can be seen from the following diagrams.



Both these latter cases have been defined as potential determining adsorption and the case (a) is evidently identical with Pauli's ionogenic process.

We must thus conclude that for colloid systems in general both specific or Gouy and potential determining adsorption can play a part in forming the interphase layer of ion pairs.

Part of our enquiry must be devoted to the interphasic layer of ion pairs. The problem of evaluation of the density of population in these cases when the Lippmann equation is not applicable is not a simple one, but several indirect methods of attack have been proposed. Again, if treated as a condenser, its capacity can be calculated. Whilst considerable variations in this quantity were found in early experiments, it is satisfactory to note that much closer agreement between various methods is obtained in more recent work. The density of population of the ion pair interphase may, of course, be varied by the presence of other non-ionisable solutes which are capillary active, and indeed, replacing water by other liquid media must affect the ion pair interphase to a marked extent. It is to be noted that all capillary active solvents must contain permanent dipoles which must be orientated at the interphase. It is a pity that the published data for interphases in non-aqueous media are so limited in extent, because by substitution in the Lippmann equation such data would provide us with a most exact method of studying the structure of this part of the double layer.

We may note that there are different methods of approach to the problem of the extent of surface ionisation of the ion pair interphase. If the extent of dissociation is small, utilising the solubility product in solution of the ion pair system as a criterion, the phenomenon of base and acid exchange may occur and the ionic concentration may be governed by a Donnan distribution. Such a treatment is probably reasonably valid for an interphase which falls into the Pauli ionogenic class, but is clearly inapplicable to the others. The Stern Debye Hückel treatment of the diffuse or dissociated fraction of the ion pair interphase leads to the correct expressions for the variation of mobility of a particle in an electric field as a function of the ionic strength and of the size of the particle, but only within certain ranges of ionic strength. At high concentrations of electrolyte where the diffuse layer thickness,  $\kappa$ , is relatively thin, mobility experiments suggest that the extent of surface ionisation is reduced, whilst with solutions of very low ionic strength the intrusion of a Donnan effect again modifies the extent of ionisation.

The stability of a colloid system is governed by the nature of approach and interaction of two polyvalent ions of large charge with their circumambient Debye-Hückel ionic atmospheres. The mathematical treatment of this case is evidently somewhat formidable, but one of the interesting conclusions which have been reached is that there is a position

of minimum energy before the two particles are actually in contact, suggesting that such systems should reveal thixotropic characteristics. We note a number of interesting developments which make use of the fact that part of the ion pair interphase is always dissociated, such as the deposition of latex, clays, oxides of the alkaline earths, the flotation of minerals, and the recent method of electrophoretic separation introduced by Tiselius which is proving so valuable in biological fields.

The study of living membranes and all surfaces reveals the existence of electrical double layers; further, that these are maintained at certain values which are dependent on the proper functioning of the sequence of enzymytic and transport reactions which are a criterion of life. It is an interesting speculation as to how far the electrical double layer itself plays a part in the dynamical equilibrium which constitutes biological processes.

The Lippmann equation reveals the effect on the interfacial free energy. An alteration in this quantity may involve a concomitant change in composition, mechanical properties, or in permeability. I might mention only the interesting changes in physical properties and phase boundary potentials of monolayers of proteins caused by lipoids, or of fatty acids by mere traces of divalent ions as examples of such an action.

My best thanks are due both to the Committee, to whose activities these papers are due, and to the contributors who have taken the trouble to complete their manuscripts under somewhat adverse and disturbed conditions.

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## PART I.—EXPERIMENTAL METHODS AND RESULTS. (A) ELECTROPHORESIS.

### MICROSCOPIC METHOD OF ELECTROPHORESIS AND ITS APPLICATION TO THE STUDY OF IONOGENIC AND NON-IONOGENIC SURFACES.

BY HAROLD A. ABRAMSON.\*

Received 21st June, 1939.

#### Microscopic Method of Electrophoresis.

At a recent meeting of the New York Academy of Sciences, I had the pleasure of meeting Dr. Risdale Ellis, who was the first investigator to make quantitative measurements of the electrical mobility of microscopically visible particles.<sup>1</sup> Ever since the time of Quincke's ingenious experimentation on the electrical mobility of microscopic particles,<sup>2</sup> lack of quantitative data retarded that field of investigation until the classical researches of Ellis. Ellis showed that the flat type of electrophoresis cell which he constructed yielded the mobility of the particle relative to the liquid when the velocity-level curve was integrated. His early data are plotted in Fig. 1 and illustrate the accuracy of his technique. Further simplification of the hydrodynamic theory applicable to flat cataphoresis cells by Smolouchowski as well as his theory of the  $\zeta$ -potential started a new era in the development of this phase of surface chemistry.<sup>3</sup>

Amongst the various electrophoresis cells which had been constructed during the period from 1911-1925 the arrangement used by Northrop and Kunitz<sup>4</sup> seemed to have excellent potentialities. The modification of the

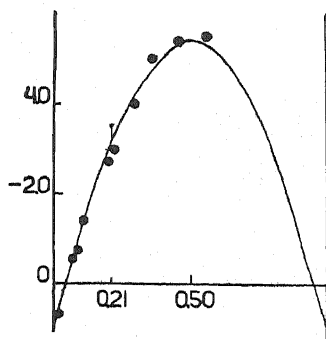


FIG. 1.—Data of Ellis showing the variations of the observed electric mobilities (ordinate) of oil droplets at different levels in a flat electrophoresis cell. The smooth curve is that predicted by hydrodynamic theory.

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<sup>1</sup> R. Ellis, *Z. physik. Chem.*, 1912, 78, 321.

<sup>2</sup> G. Quincke, *Pogg. Ann.*, 1861, 113, 513.

<sup>3</sup> M. Smolouchowski, in Graetz, *Handbuch der Elektrizität und des Magnetismus* Barth, Leipzig, Vol. II, 1921, p. 366.

<sup>4</sup> J. H. Northrop and M. Kunitz, *J. Gen. Physiol.*, 1925, 7, 729.



Northrop-Kunitz cell which has been employed by the writer since 1929 is illustrated in Fig. 2.<sup>5</sup> This cell is constructed of one piece of glass and can be readily cleaned with sodium hydroxide, dilute acid, and cleaning fluid. The instrument rests directly on the stage of the microscope and can be inverted to resuspend particles which have settled. The construction of the side arms permits the introduction of plaster of Paris plugs into the electrode vessels. These plugs prevent precipitation of protein by diffusion of the copper sulphate from the electrode compartment into the side arm. Because of the

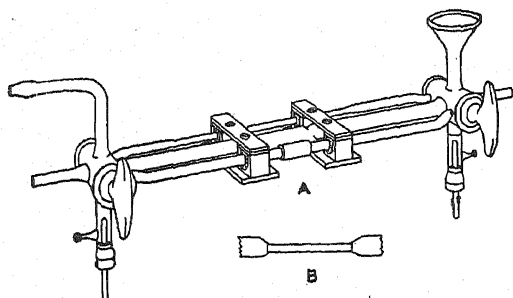


FIG. 2.—Flat cell for microscopic electrophoresis.

non-polarisability of the electrodes the technique is well adapted for use in biological systems. The vertical model of this type of cell is illustrated in Fig. 3.<sup>6</sup> In both types of cells the field strength can be readily computed by applying Ohm's law. The theory of Smoluchowski for the streaming of the liquid in cells of this type has been published in sufficient detail elsewhere.<sup>7</sup> To the uninitiated a perusal of the summary published by Professor L. S. Moyer<sup>8</sup> on the measurement of microscopic electrophoresis may be mentioned. However, it is important to recall that the width of the flat cell must be great compared with the thickness. Since the observed mobility is equal to the mobility of the particle plus that of the liquid due to electro-osmosis along the walls, a suitable correction must be introduced for the side walls if they are too near to one another. Komagata<sup>9</sup> has shown that if the cell is wide enough the theory of Smoluchowski obtains. When this does not hold the following equation permits the stationary level to be found:

$$\gamma(V_w=0) = \pm b \sqrt{\frac{1}{3} \left( 1 + \frac{384}{\pi^5 k} \right)}.$$

Here  $\gamma$  is the level measured from the central axis and  $k$  is the ratio of one-half the width to one-half the depth,  $b$ .

As far as the writer is aware, the flat electrophoresis cells illustrated in Figs. 2 and 3, are the only instruments which have been directly shown to yield values of the electrical mobility comparable with those obtained in

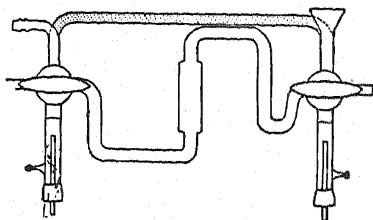


FIG. 3.—Vertical cell for microscopic electrophoresis.

<sup>5</sup> H. A. Abramson, *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chemical Catalog Co., New York, 1934, Chap. 3. H. A. Abramson, *J. Gen. Physiol.*, 1928, 12, 469. H. A. Abramson, *ibid.*, 1930, 13, 657. H. A. Abramson and E. B. Grossman, *ibid.*, 1931, 14, 563.

<sup>6</sup> Abramson, Moyer and Voet, *J. A. Chem. Soc.*, 1936, 58, 2362.

<sup>7</sup> See references 5, 8, 21.

<sup>8</sup> L. S. Moyer, *J. Bach.*, 1936, 31, 531.

<sup>9</sup> S. Komagata, *Researches Electrotech. Lab. Tokyo*, No. 348, 1933. See also G. S. van Gils, *Electrophorese metingen.*, Thesis, Utrecht, 1936.

U-tubes.<sup>10</sup> They may, therefore, be used as standards in calibration of other cells. Presumptive evidence that the method of microscopic electrophoresis agrees with the moving boundary method was shown by the comparison of the movement of quartz particles covered with serum albumin and the dissolved protein itself. Another test lies in recent measurements of Howitt.<sup>11</sup> Howitt compared the values for the electrical mobilities of red cells obtained by the writer who used the microscopic method with data found by his own method, a U-tube previously employed in the measurements of protein by Prideaux and Howitt.

TABLE I.—COMPARABLE MOBILITIES ( $\mu$ /sec.) OF RED BLOOD CELLS FOUND BY DIFFERENT OBSERVERS WITH SEVERAL TYPES OF INSTRUMENTS.

	Man.	Rat.	Rabbit.	Mouse.	Guinea Pig.
Moving boundary . . . .	—	1.45	0.60	1.42	1.16
Horizontal . . . . .	1.31	1.45	0.55	1.35	1.11
Horizontal . . . . .	1.30	—	—	—	—
Vertical . . . . .	1.25	—	—	—	—

In Table I are electrical mobilities of blood cells which illustrate the agreement within the usual limit of error between the moving boundary and the microscopic methods.

Although in certain systems, the accuracy of the method of microscopic electrophoresis may lie within 3 per cent., in many instances, especially in the presence of relatively high concentrations of electrolytes, the error may reach 10 per cent. and devices capable of increasing the precision would be desirable. A new technique described by Smith and Lisse<sup>12</sup> may supply this need. Smith and Lisse employed two tubes in parallel,  $T_1$  and  $T_2$  (see Fig. 4) a closed system between platinum electrodes. The relationship between the tubes is so fixed that the electro-osmotic return flow ordinarily taking place in the mid-regions of a single tube microelectrophoresis cell, takes place in the tube  $T_2$  of larger radius. Further, there is no movement of the liquid along the axis of the tube of smaller radius. Hence the velocity in the centre of  $T_1$  (depth =  $\frac{1}{2}$ ) corresponds to the velocity of the particle relative to the liquid. The stationary level is then at the centre of the cell. The velocity gradient is 0 at this level. In the single cell of cylindrical cross-section, the velocity relative to the liquid is at the level 0.146 (0.854) while here there is only one stationary level. The development of this technique and further evidence that it provides quantitative data would make it more desirable to employ it than a single cell.

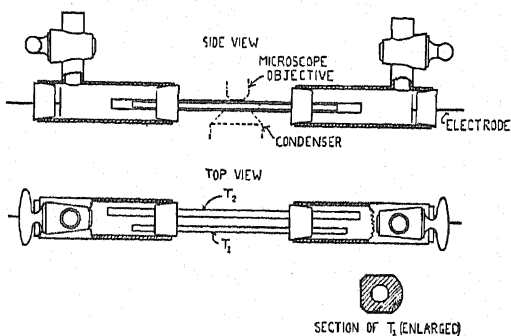


FIG. 4.—Two-cell system for microscopic electrophoresis of Smith and Lisse.

<sup>10</sup> H. A. Abramson and L. S. Moyer, *Trans. Electrochem. Soc.*, 1937, **71**, 135.

<sup>11</sup> F. O. Howitt, *Biochem. J.*, 1934, **28**, 1165.

<sup>12</sup> M. E. Smith and M. W. Lisse, *J. Physical Chem.*, 1936, **40**, 399.

In connection with electrophoresis cells of circular cross section, aside from difficulties in focussing, it has been shown by Boswell and Larson<sup>13</sup> that certain optical difficulties may be encountered in finding the stationary level. If the lighting is from one side, a beam entering at the stationary level will be bent upward to a depth of 0.195 times the radius from the top and hence will give an erroneous measurement if the microscope is focussed on the beam. The difficulties in focussing in microscopic cells of this type have been discussed in more detail in a recent communication by Henry.<sup>14</sup> The error in focussing, as Henry points out, is so great, that conclusions hitherto drawn by many investigators using the cell of circular cross section without correcting for depth, may require revision. Henry's correction, of course, does not apply to the flat electrophoresis cell. The use of data of White and co-workers<sup>15</sup> (who used cells of cylindrical cross-section primarily) to support<sup>16</sup> a point of view emphasising the importance of relaxation forces is not justified for the following reason. White found contrary to the data of Abramson,<sup>17</sup> Daniel,<sup>18</sup> Moyer,<sup>19</sup> Bull<sup>20</sup> for proteins, and Sumner and Henry<sup>21</sup> for wax, that the ratio of electrophoresis to electro-osmosis was greater than 1.0. White apparently neither used the Henry correction in focussing, nor employed a sufficient concentration of proteins to form complete films, according to the viewpoint of Moyer and the writer. We re-emphasise that, experimentally, where complete films of protein are formed, the ratio of electrophoresis to electro-osmosis is 1.0.

In view of the precision obtainable by means of the flat electrophoresis cell it is desirable to discuss at this time some of the data which have been obtained by the writer and others with cells of this type.

### Ionogenic Amphoteric Surfaces.

Changes in the polar groups of organic ampholytes incidental to surface formation may be subdivided into three divisions by interpretation of electrophoretic data:

*Group (1).* This group comprises proteins after adsorption by quartz and other surfaces with little or no change in the number and orientation of the acid and basic groups.

*Group (2).* This group, as group 1, is essentially composed of proteins with slight changes in number and orientation of polar groups.

*Group (3).* More obvious changes in the nature of the orientation and in the number of polar groups are observed. Typical of this group are the surfaces of amino acid crystals.

*Group 1.* The first comparison of the electric mobility of a dissolved protein and that of an adsorbed protein under similar condition was made by the writer in 1932.<sup>22</sup> In Fig. 5 are given the data of Tiselius<sup>23</sup> for the dissolved form of horse serum albumin and the data obtained

<sup>13</sup> A. M. Boswell and T. E. Larson, *J. Physical Chem.*, 1936, **40**, 833.

<sup>14</sup> D. C. Henry, *J. Chem. Soc.*, 1938, 997.

<sup>15</sup> H. L. White, B. Monaghan and F. Urban, *J. Physical Chem.*, 1935, **39**, 611.  
H. L. White and B. Monaghan, *ibid.*, 925. H. L. White and Fourt, *ibid.*, 1938, **42**, 29.

<sup>16</sup> Hermans, *Phil. Mag.*, 1938, **26**, 650.

<sup>17</sup> H. A. Abramson, *J. Gen. Physiol.*, 1932, **16**, 1.

<sup>18</sup> J. Daniel, *ibid.*, 1933, **16**, 457.

<sup>19</sup> L. S. Moyer and H. A. Abramson, *ibid.*, 1936, **19**, 727. L. S. Moyer, *J. Physical Chem.*, 1938, **42**, 391. L. S. Moyer, *Trans. Electrochemical Soc.*, 1938.

<sup>20</sup> H. B. Bull, *J. Physic. Chem.*, 1935, **39**, 577.

<sup>21</sup> C. G. Sumner and D. C. Henry, *Proc. Roy. Soc. A*, 1931, **133**, 130.

<sup>22</sup> H. A. Abramson, *J. Gen. Physiol.*, 1932, **15**, 575.

<sup>23</sup> A. Tiselius, Dissertation, Uppsala, 1930.

by the writer and Moyer<sup>24</sup> for quartz and collodion particles, respectively, coated with a film of this protein. Note that all the points fall together on a smooth curve. The electric mobilities of this protein dissolved (0.02 M. acetate buffer) are the same as the electric mobilities of quartz and collodion particles covered with the complete protein films. Neither the size nor the nature of these particles covered with films of this protein influences the electric mobility of the protein covered particles.<sup>25</sup> The ratio of the electrophoretic mobility of the protein covered particle to the electro-osmotic mobility of the liquid along flat surface covered with the same protein is equal to 1.0. Indeed the mobility of particles of this type is independent not only of the size, but also of the shape and orientation of the particle.<sup>25</sup> In order for the electric mobility to remain the same after adsorption of the protein either the charge density and the radius must change in a way exactly to compensate one another or else they must remain essentially the same after adsorption as they were in the dissolved state. This maintenance of constant electric mobility for a single dissolved molecule and the adsorbed film could hardly be achieved by a compensation mechanism. It is necessary to conclude in this instance that, following the adsorption of a protein like serum albumin, there was no important change in the orientation or activity of the carboxyl or amino groups incidental to the adsorption of the protein and the formation of the complete film.<sup>22</sup> Furthermore, a great degree of distortion of the molecules of the outermost layer of protein film could not have occurred. That is, the effective radii of curvature of the adsorbed protein molecules are essentially the same as the effective radii of curvature of the dissolved molecules themselves.

A comparison of the data of dissolved pseudoglobulin<sup>26</sup> (Tiselius) with data for globulin films on collodion particles<sup>27</sup> reveals the same remarkable constancy of electric mobility from pH 4 to pH 8 (Fig. 6). This protein and serum albumin are the only ones for which data are

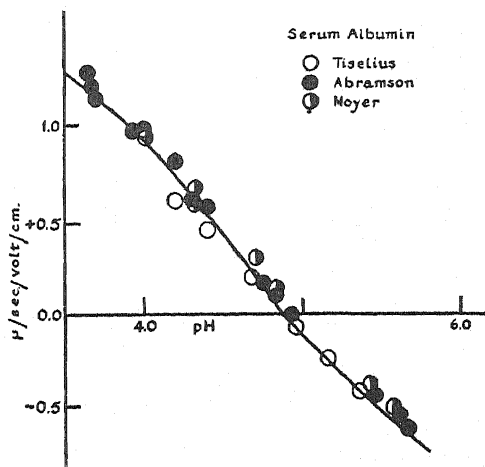


FIG. 5.—The electric mobility of horse serum albumin, as a function of pH in 0.02 M. acetate buffers at 20° C. The smooth curve was drawn freehand. There is no significant difference between the data for adsorbed and dissolved protein.

<sup>24</sup> L. S. Moyer and H. A. Abramson, *J. Biol. Chem.*, 1938, **123**, 391.

<sup>25</sup> H. A. Abramson, *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chemical Catalog Co., New York, 1934, pp. 111-122.

<sup>26</sup> A. Tiselius, *Biochem. J.*, 1937, **31**, 313, and reference <sup>23</sup>.

<sup>27</sup> L. S. Moyer, *Symposia on Quantitative Biology*, Cold Spring Harbor, 1938, **6**, 228. See also reference <sup>24</sup>.

available for exact comparison of the dissolved and adsorbed forms, although indirect evidence is available for gelatin.<sup>22, 18</sup>

**Group 2.** In the case of egg albumin the electrophoretic behaviour of the adsorbed film differs slightly but definitely from that of the

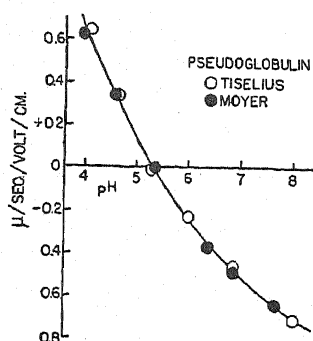


FIG. 6.—The electric mobility curve of horse serum pseudoglobulin. Notice that a single curve fits the data for dissolved and adsorbed protein.

molecules of the solution. The results of Moyer,<sup>28</sup> Tiselius, and the writer,<sup>22</sup> are shown in Fig. 7. A discussion of the discrepancy between the points of Abramson and the smooth curve of Moyer may be found elsewhere. It is evident that the electrokinetic properties of air denatured egg albumin are considerably different from those of molecules of egg albumin solution. The differences in the isoelectric point may be correlated with changes in relative strengths of the acidic and basic group incidental to denaturation as well as alterations in the shape of the molecule.

Some difficulty may be encountered in classifying the electrokinetic behaviour of insulin crystals which differs

from the behaviour of insulin films adsorbed on to quartz. The isoelectric point of one preparation of insulin crystals studied by Wintersteiner and Abramson<sup>29</sup> differed from that of the adsorbed film of insulin by approximately 0.35 pH units. On the basis of the state

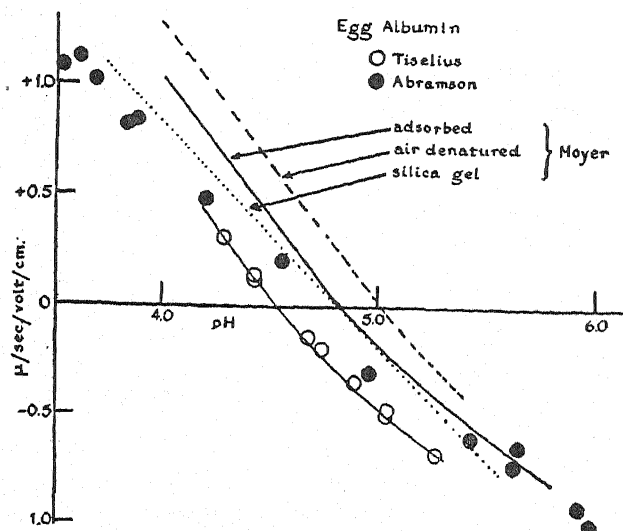


FIG. 7.—Comparison of the data of Tiselius for dissolved egg albumin with results of the writer and of Moyer for adsorbed films of this protein.

of aggregation a better classification would, perhaps, include insulin crystals in the group of amphoteric crystals, the amino acids, now to be discussed.

<sup>28</sup> L. S. Moyer, *J. Physic. Chem.*, 1938, 42, 71. L. S. Moyer and J. Abels, *J. Biol. Chem.*, 1937, 121, 331. See also reference <sup>27</sup>.

<sup>29</sup> O. Wintersteiner and H. A. Abramson, *ibid.*, 1933, 99, 741.

*Group 3.* The electrokinetic properties of amino acid crystals furnish data for a third type of behaviour, the very different isoelectric point and mobilities of dissolved crystalline amino acid. The electric mobilities of crystals of aspartic acid, cystine, and tyrosine were determined over a wide range of  $pH$ . The data are summarised in Fig. 8.<sup>29</sup> The differences between the isoelectric points of dissolved and crystalline amino acids range from 0.5  $pH$  unit, as in the case of aspartic acid, to more than 3.0  $pH$  units as in the case of tyrosine. In contrast note that the isoelectric point of the crystals of the three substances are very close together (at about  $pH$  2.4) while those of the corresponding dissolved amino acids are much further apart. There are no inflections at the isoelectric point. The significant shift of the isoelectric points of the surface of the amino acid crystals is probably not to be explained simply by a corresponding change in the relative strength of the acidic and basic groups, although large changes in the relative strengths of these groups may occur. The surface charge may be influenced significantly by the other ions (amino acid, etc.) present in the medium.

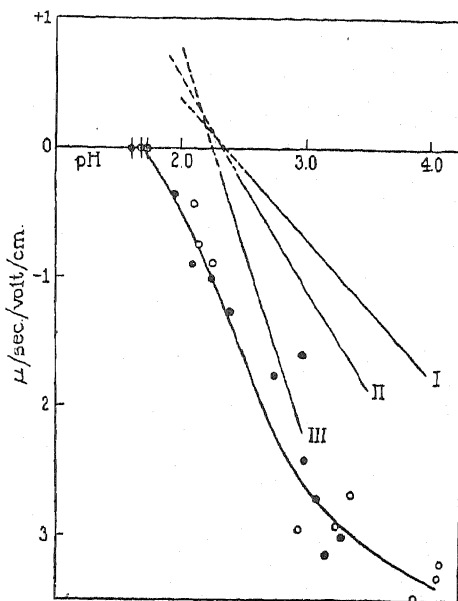


FIG. 8.—A comparison of the electric mobilities of the surfaces of crystalline amino acids with emulsion droplets of simple alkyl-benzenes. 1, 2, and 3 are cystine, tyrosine, and aspartic acid crystals respectively, whereas, the smooth curve drawn through the points represents the behaviour of *n*-propyl benzene and ethyl benzene.

### Titration Curves and Electric Mobility.

Investigations<sup>22, 18, 24, 28</sup> showing that a direct proportionality may exist between titration curves (acid and base bound) and the electric mobility of proteins in simple systems have furnished a basis for further applications of electrokinetic data to the investigation of the nature of surfaces of protein molecules and of adsorbed films of protein (Fig. 9). According to the Debye-Henry theory<sup>30</sup> the electrical mobility of the spherical protein ion is given by the equation,

$$v = \frac{Qf(\kappa r)}{6\pi\eta(\kappa r + 1)}, \quad \dots \dots \dots (I)$$

where  $v$  is the electrical mobility;  $Q$  is the net charge per ion;  $\kappa$  that value in the Debye expression;  $r$  is the radius of a spherical particle;

<sup>30</sup> D. C. Henry, *Proc. Roy. Soc., A*, 1931, 133, 106.

and  $\eta$  is the coefficient of viscosity. Having demonstrated that the mobility under certain conditions is proportional to  $\epsilon$  the number of

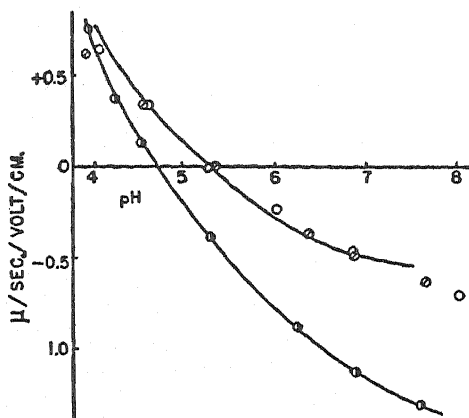


FIG. 9.—Electric mobility and titration curves of serum albumin and pseudo-globulin. These curves illustrate that from pH 4 to 8 the electric mobilities of these proteins is proportional to their combining power with  $H^+$  and  $OH^-$  ions in the range investigated.

equivalents of hydrogen and the hydroxyl ions found per mole of protein, it immediately follows that the average of the charge,  $Q$ , in the protein molecule is given by

$$Q = e\epsilon,$$

where  $e$  is the electronic charge. In the derivation of equation (1), the ions in the ion atmosphere are implicitly assumed to be point charges. Gorin<sup>31</sup> has studied the effect of this assumption on the hydration of protein. He comes to the conclusion that rather than the simple form of the Debye equation given in equation (1), the

$\zeta$ -potential of particles of that type is given by

$$\zeta = \frac{Q(1 + \kappa r_i)}{Dr_p[\kappa(r_p + r_i) + 1]} \quad (2)$$

( $r_p$  is the radius of the protein;  $r_i$  is an "average" radius of the ions in the double layer). This equation differs significantly from equation (1) in the numerator term  $(1 + \kappa r_i)$  which is independent of the size of the protein. The value of this theory is well illustrated by his calculation of the radius of certain proteins. From the ratio of the mobilities at two ionic strengths it can readily be shown that,

$$v_1/v_2 = b = \frac{(\kappa_2 r + \kappa_2 r_i + 1)}{(\kappa_1 r + \kappa_1 r_i + 1)} \left( \frac{1 + r_i \kappa_1}{1 + r_i \kappa_2} \right).$$

In Table II is a comparison of the theoretical equation of Gorin with the empirical equations used hitherto. Gorin's theory fits the data very well indeed. It may be noted that Gorin has subsequently confirmed his values of  $r_i$ , given in Table II. In one sense

TABLE II.—COMPARISON OF THE THEORETICAL AND EMPIRICAL EQUATIONS.

Protsin.	Radius, in $m\mu$ , Calculated from		
	Theory		Empirical Equation $a = 2$ .
	$r_i = 0.2$ .	$r_i = 0.3$ .	
	$m\mu$ .	$m\mu$ .	$m\mu$ .
Egg albumin . . .	1.6	2.0	2.2
Serum albumin . . .	2.7	3.4	3.4
R-phycoerythrin . . .	3.6	6.4	5.2

<sup>31</sup> M. Gorin. See H. A. Abramson, M. Gorin and L. S. Moyer, *Chem. Reviews*, April, 1939, 24, No. 2. See also M. Gorin, *J. Chem. Physics*, June, 1939.

equation (2) of Gorin is restricted because it is for spherical particles. It finds its greatest usefulness in studying the same particle at two values of the ionic strength in studies of the type indicated in Table II. Within the narrow range of ionic strength considered in Table II, Gorin has attempted to study the shape factor by making preliminary estimations of the electrokinetic potential of an aspherical protein molecule by using a simplified model. According to Gorin, for long cylinders, neglecting the ends, the  $\zeta$ -potential is a function of the radius and ionic strength,

$$\zeta = \frac{2QK_0(\kappa a)}{Dl\kappa aK_1(\kappa a)} + \frac{2Q}{Dl} \ln \left( \frac{a + r_i}{a} \right),$$

where  $Q$  is the net charge,  $D$  is the dielectric constant of the medium,  $l$  is the length of the cylinder, and  $a$  is its radius. The function  $K_0$  and  $K_1$  are special solutions of the modified Bessel's equation of zero and first order which are discussed in detail elsewhere. The electric mobility becomes

$$v = \frac{2QK_0(\kappa a)}{F\pi\eta l\kappa aK_1(\kappa a)} + \frac{2Q}{F\pi\eta l} \ln \left( \frac{a + r_i}{a} \right).$$

The relationship between the  $\zeta$ -potential and the electrical mobility of long cylinders was obtained by Gorin from the theory of Henry. The combination of Gorin's equation with Henry's theory leads to an expression from which may be calculated the asymmetry of protein molecules. See Table III.

TABLE III.—ASYMMETRY FROM ELECTROKINETIC DATA FOR CYLINDRICAL MODEL.

Protein.	Length/Breadth.	
	Electrokinetic Data.	Perrin's Equation and Svedberg's Data.
Egg albumin . . .	4.4	2.6
Serum albumin . . .	6.3	5.7
"Globulin" . . .	7.3	7.6

### Surfaces Essentially Non-Ionogenic.

In the case of protein molecules or of protein surfaces the comparatively large numbers of amino and carboxyl radicals primarily determine the net charge of the protein under ordinary conditions. That is, the hydrogen ion activity of the medium determines the net charge in the absence of high concentrations of electrolytes. When simple electrolytes are present in sufficient quantity it is not the general nature of the mobility- $pH$  curve of the protein which is changed but rather its position which may be altered with a shift in the isoelectric point and with a decrease in the absolute values of the mobility. As has been discussed elsewhere,<sup>32</sup> the ideal protein has an isoelectric point unchanged by the addition of salt. The understanding of the charging process of non-ionogenic surfaces like quartz, paraffin oil, or air bubbles is not as simple as that for the ideal protein. The charge density,  $\sigma$ , of surfaces of the non-ionogenic group is primarily dependent upon the

<sup>32</sup> H. A. Abramson, *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chemical Catalogue Co., New York, 1934, p. 292. See also H. A. Abramson, *J. Physical Chem.*, 1935, 39, 749.



concentration,  $c$ , of salt present in the medium and the hydrogen ion activity plays a less important rôle. It is important to distinguish between the effect of salt on the electrical mobility,  $v$ , of surfaces of this type and the charge density,  $\sigma$ .

The usual effect of salts on the electrical mobility of particles of any type is complicated in dilute solutions by the presence of peculiar maxima which have been observed very frequently. Considerations of the problem indicate that the charging process of the surface must be considered if the maxima are to be explained at all. The charge of the simple ion, like sodium ion, remains constant even though its mobility decreases as the ionic strength increases. In the case of a non-ionogenic surface another situation exists. As the concentration of salts increase, the net surface charge density changes as more ions are added to the solution, and by means of the following equation  $\sigma$  may be calculated:

$$\sigma = \sqrt{\frac{NDkT}{2\pi \times 1000}} c_{1[2]z_1[2]} \left[ \frac{1}{z_2} \left( e^{+z_2 \frac{e\zeta}{kT}} - 1 \right) + \frac{1}{z_1} \left( e^{-z_1 \frac{e\zeta}{kT}} - 1 \right) \right]$$

where  $N$  is Avogadro's number,  $k$  Boltzmann's constant,  $c$  the molar concentration,  $e$  the base of the natural logarithm,  $e$  the electronic charge  $z$  the valence, and  $T$  the absolute temperature. In case  $z_1 = -z_2 = z$  in aqueous media, equation reduces to

$$\sigma = 2\sqrt{\frac{NDkT}{2\pi \times 1000}} \sqrt{c} \sinh z \frac{e\zeta}{kT}.$$

We have, then, a means of following changes in the charge density as the concentration of salt increases.<sup>33</sup> Keeping in mind the complex form of the  $\zeta - c$  curve, examine the diagrams given in Fig. 10, which illustrate for a variety of surfaces what occurs when the density of net charge is calculated.<sup>34</sup> The characteristic of the  $\sigma - c$  curve in every instance is that with the addition of salts, not reversing the sign of charge,  $\sigma$  increases sharply and almost linearly in low concentrations with the charge density approaching a limiting value at about 0.001 M. The descending part of the mobility concentration curve observed in solutions where  $\sigma$  approaches its limiting value, has frequently been taken to represent a discharge of the surface of the particle since aggregation frequently occurs in this range of concentration. Fig. 10 demonstrates, however, that contrary to this notion the addition of salt is actually accompanied by an increase in net charge even in the region where it is known that rapid coagulation may occur. The shape of the mobility concentration curve may be due to the fact that the mobility

<sup>33</sup> L. Gouy, *J. Physique*, 1910, 9, 457. A. Gyemant, *Grundzüge der Kolloidphysik*, Vieweg, Braunschweig, 1925, p. 75. H. Müller, *Kolloidchem. Beih.*, 1928, 26, 257. M. Mooney, *J. Physical Chem.*, 1931, 35, 331, and personal communications. H. A. Abramson and H. Müller, *Bull. Am. Physical Soc.*, 1932, 7, 11. *Symposia on Quantitative Biology*, Cold Spring Harbor, Darwin Press, New Bedford, 1933, 1, J. Bikerman, *Z. physik. Chem., A*, 1933, 163, 378.

<sup>34</sup> H. A. Abramson and H. Müller, *Bull. Am. Physical Soc.*, 1932, 7, 11, where the general form and nature of the  $\sigma - c$  curves were presented apparently for the first time. *Symposia on Quantitative Biology*, Cold Spring Harbor, Darwin Press, New Bedford, 1933, 1. H. A. Abramson, *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chemical Catalog Co., New York, 1934, pp. 184, 188, 194, 204, 205, 210, 228, 240, 242, 290, 302. See also L. S. Moyer, *J. Bacteriol.*, 1936, 32, 433. L. S. Moyer and H. B. Bull, *I. Gen. Physiol.*, 1935, 19, 239.

depends upon two variables both of which depend upon the concentration in different ways:

(1) the way in which  $\sigma$ , the charge density of the surface depends on the concentration, and

(2) the way in which  $\kappa$ , the reciprocal thickness of the diffuse ion atmosphere depends on the concentration. As  $c$  increases  $1/\kappa$  decreases.

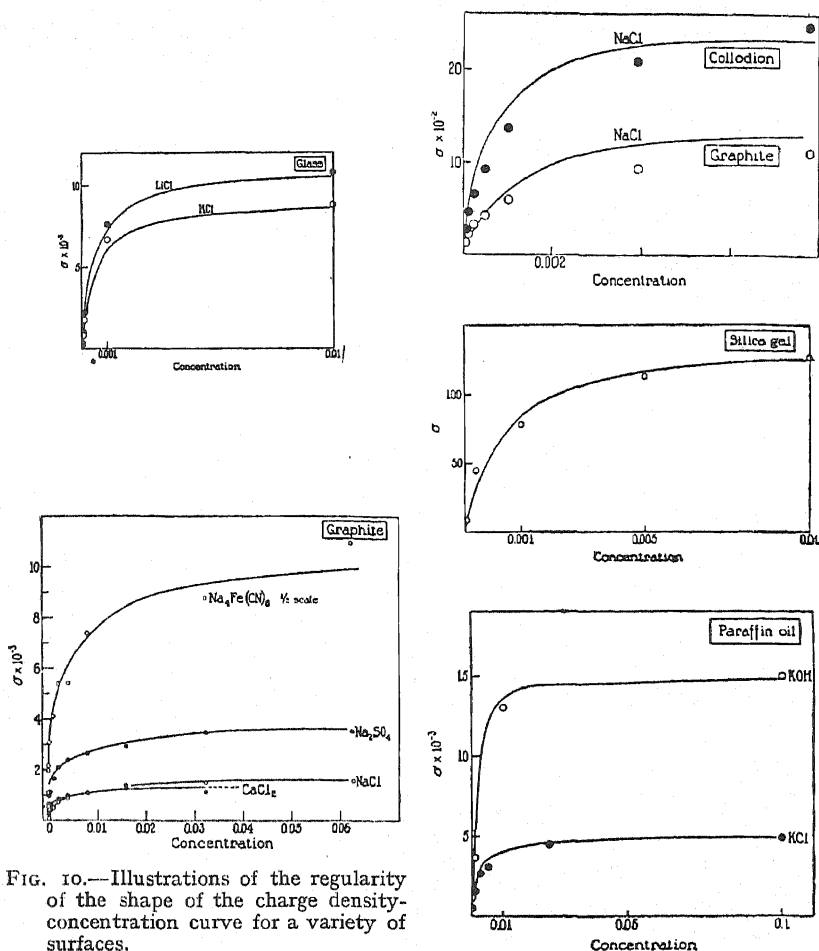


FIG. 10.—Illustrations of the regularity of the shape of the charge density-concentration curve for a variety of surfaces.

When  $c$  is small the increase in  $\sigma$  is more important than the decrease in  $1/\kappa$ . That is, at low concentrations of salt, the charging process by the ions is more important than the diminution of the thickness of the electric double layer. But if the concentration of salt increases further, the decrease in the thickness of the double layer becomes more important in flattening out the  $\sigma - c$  curve as saturation occurs by what we take to be selective ionic adsorption.

# THE INFLUENCE OF ELECTROLYTE CONCENTRATION ON THE ELECTROPHORETIC MOBILITY OF EGG ALBUMIN.

BY ARNE TISELIUS AND HARRY SVENSSON.

*Received 30th June, 1939.*

Much work has been done on the influence of salts upon the electrophoresis of colloidal particles of sufficient size to make direct microscopic or ultra-microscopic observation of the migration possible. On the other hand very little is known concerning the effects of variations in salt concentration on the mobilities of colloids with smaller particles, including the proteins. This is due to the fact that mobility measurements on these substances, for which moving boundary or transference methods alone are available, are more laborious and time consuming. Moreover, certain technical difficulties present themselves when measurements have to be made over a wide range of salt concentrations.<sup>1</sup> The problem is of interest, however, for several reasons. Electrophoretic data are of increasing importance for studies of the homogeneity of these substances and for their characterisation, but so far the relationship between the mobility and the more fundamental properties of the molecule, including the charge and size and also the composition of the medium have not been subjected to the detailed experimental investigation desirable for comparison with theoretical formulæ for electrophoresis. There are certain advantages in employing the proteins for such purposes, because extensive series of observations of the size and the frictional constants of protein molecules are now available, thanks to the work of Svedberg and his collaborators. Moreover, the recent work of Adair and Adair<sup>2</sup> has made it possible to estimate the charge of protein molecules from measurements of membrane potentials. The calculation of the apparent charge of a protein molecule from a mobility determination and an estimation of the frictional constant from combined sedimentation velocity and equilibrium data has been described elsewhere.<sup>3</sup> The ionic atmosphere round the particle will, however, tend to make the apparent charge smaller than the actual charge. An attempt was also made to calculate the latter from the former by the equation given by Debye and Hückel.

The calculation of the frictional constant can now be made more directly and accurately from the equation  $D = RT/f$ , using the accurate values for the diffusion constant  $D$  determined by the method of

<sup>1</sup> The possible sources of error in measurements by the moving boundary method, especially the boundary anomalies at low salt concentrations, have been discussed in detail elsewhere. See, for example: Tiselius, *Nova Acta Reg. Soc. Scient. Upsal.*, 1930, Ser. IV, Vol. 7, No. 4; Henry and Brittain, *Trans. Faraday Soc.*, 1933, 29, 798; Hartley and Moilliet, *Proc. Roy. Soc.*, 1933, 140, 141; Tiselius, *Trans. Faraday Soc.*, 1937, 33, 524; Longsworth and McInnes, *Chem. Rev.*, 1939, 24, 271.

<sup>2</sup> Adair and Adair, *Biochem. J.*, 1934, 38, 199, 1230.

<sup>3</sup> Tiselius, *Nova Acta Soc. Scient. Upsal.*, 1930, Ser. IV, Vol. 7, No. 4 (Dissertation).

Lamm.<sup>4, 5</sup> This procedure was used in the following. Protein solutions containing strong acids or bases are not suitable for experiments of this kind, as the  $pH$  usually is outside the stability region of the protein molecule. The experiments to be described here were therefore made in buffered solutions within this region.

Egg albumin was used for all the experiments, being a well defined protein with approximately spherical molecules, the frictional ratio being 1.1. It was prepared in the usual way and recrystallised three times. We are indebted to Mr. Kjell Andersson for this preparation.

The improved electrophoresis apparatus earlier<sup>6</sup> described was used throughout the investigation. The main advantages of this construction are: (1) the reduction of the disturbing effects of heat convection in the electrophoresis tube by working at a temperature in the neighbourhood of  $+4^{\circ}C$ ; (2) convenient optical observation of the migrating boundaries by the Toepler Schlieren method or similar methods depending upon the refractive index; (3) an improved method for making the boundary and dividing the contents of the electrophoresis tube into portions for analysis; (4) a compensation arrangement for preventing the boundaries from migrating out of the tube in prolonged experiments, particularly valuable for separation purposes. The measurements were carried out at  $+0.5^{\circ}C$ .

Two series of measurements were made, one at a  $pH$  fairly distant from the isoelectric point, one in its immediate neighbourhood, with the purpose of studying the influence of electrolyte concentration on its position.

### Measurements at $pH$ 7-10.

As the  $pH$  of a buffer of constant composition varies with its concentration, two experiments were made for each ionic strength, with a  $pH$  difference of about 0.4  $pH$  units, and the mobility at  $pH$  7-10 was calculated from these by interpolation. The mobility- $pH$  curve is approximately a straight line in this region. The ionic strength was varied between 0.200 and 0.002. In the extremely weak buffer solutions used in some of the experiments, the  $pH$  and conductivity differences between protein and supernatant solutions may be considerable, which causes boundary anomalies and unsymmetrical migration. We have therefore chosen a quite low protein concentration (0.22 per cent.). Even with this low protein concentration boundary anomalies may be considerable with the most dilute buffer solutions.

The results of this series are given in Table I and Fig. 1. The column "ionic strength for protein solution" in this table requires some discussion. In the stronger buffer solutions the ionic strength can be calculated on basis of the stoichiometric electrolyte composition only, but at low concentrations the contribution of the sodium proteinate to the total ionic strength cannot be neglected. It has been assumed<sup>7</sup> that one  $z$ -valent protein ion makes the same contribution to the ionic strength as  $z$  univalent ions. Our calculation of the figures given in Table I, column 2, is based on this assumption. The valence of the protein ion has been obtained from the membrane potential measurements of Adair and Adair.

If the mobility  $u$  is plotted against the ionic strength  $I$ , the curve becomes extremely steep at the lowest ionic strengths. Instead, in Fig. 1,  $\sqrt{I}$  has been taken as abscissa, as is common in the various applications

<sup>4</sup> Lamm, *Nova Acta Soc. Scient. Upsal.*, 1937, Ser. IV, Vol. 10, No. 6 (Dissertation).

<sup>5</sup> Lamm and Polson, *Biochem. J.*, 1936, 30, 528.

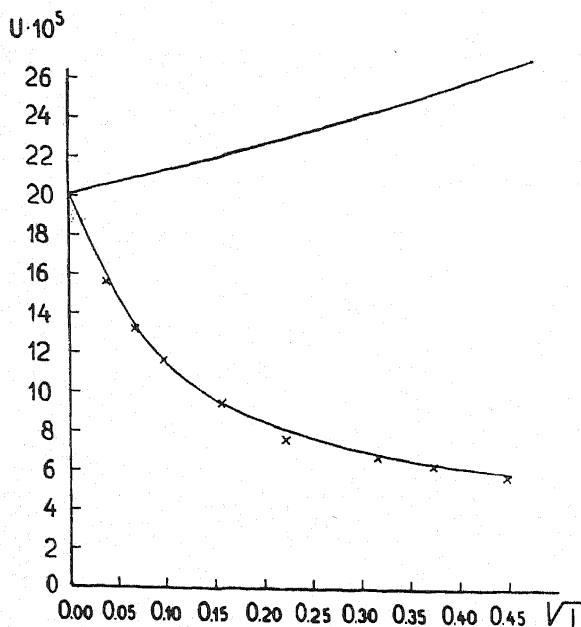
<sup>6</sup> Tiselius, *Trans. Faraday Soc.*, 1937, 33, 524.

<sup>7</sup> See, for example, Linderström-Lang, *ibid.*, 1935, 31, 324.

## 18 THE INFLUENCE OF ELECTROLYTE CONCENTRATION

TABLE I.—MOBILITY OF EGG ALBUMIN AT  $+0.5^{\circ}$  IN PHOSPHATE BUFFER SOLUTIONS OF  $pH$  7.10 AND VARYING IONIC STRENGTHS.

Ionic Strength $I$ for		$\sqrt{I}$ for Protein Solution.	$pH$ for Protein Solution.	Mobility $\times 10^6$ .	
Buffer Solution.	Protein Solution.			At the Actual $pH$ .	Interpolated to $pH$ 7.10.
0.200	0.200	0.448	6.87 7.36	5.55 5.85	5.70
0.140	0.140	0.374	6.94 7.42	6.05 6.71	6.29
0.100	0.100	0.316	6.98 7.06 7.45	6.46 6.64 7.45	6.70
0.050	0.0494	0.222	7.05 7.50	7.50 8.39	7.60
0.025	0.0244	0.156	7.11 7.52	9.49 10.81	9.45
0.010	0.00941	0.097	7.14 7.55	11.7 13.04	11.6
0.005	0.00442	0.0665	6.98 7.20 7.48	12.8 13.5 14.4	13.2
0.002	0.00143	0.038	6.96	15.1	15.6

FIG. 1.—Mobility of egg albumin at  $pH$  7.10  $t = 0.5^{\circ}$  and varying ionic strengths. Upper curve: ideal mobility, calculated on the assumption of free ionic migration. Lower curve: calculated mobilities on basis of the Debye-Hückel-Henry theory. The crosses represent the observed values.

of the Debye-Hückel theory. The points are the experimental values, the upper curve represents the ideal mobilities as calculated from the valence on the assumption that there is no double layer, the lower curve has been calculated from the valence on basis of the Debye-Hückel-Henry theory (see further below).

For the purpose of such calculations additional measurements are necessary, including the size and valence of the protein ions. A value of 45,000 has been adopted for the molecular weight of the dry protein, as the mean of figures deduced from measurements of sedimentation velocity<sup>5, 8</sup> and osmotic pressure.<sup>9</sup> The radius of the particle, including water of hydration has been taken as  $27.5 \times 10^{-8}$  cm., the calculation being based upon measurements of diffusion and crystal density.<sup>5, 10</sup> Preliminary calculations of the valence were made from the data on the base-binding capacity of egg albumin of Kekwick and Cannan.<sup>11</sup> A measurement of the base-binding capacity alone is not sufficient, however, to determine the valence in the presence of buffer mixtures, where a number of ions are present which may combine with the protein. Measurements of the membrane potentials provide a means of determining the valence of the protein ions in the presence of buffer mixtures, as shown by Adair and Adair,<sup>2</sup> who, as the result of a discussion of our results, kindly undertook to measure the membrane potentials and base-binding capacity of egg albumin under the same experimental conditions (protein concentration, temperature, salt concentrations) as had been used in the mobility determinations. The detailed results will be published elsewhere; for the present purpose it is sufficient to quote the values obtained by interpolation for  $pH$  7.10. With buffers of ionic strengths of 0.01, 0.02, 0.05 and 0.20 respectively, the valences were 12.0, 12.6, 13.1 and 15.1 respectively. The valence increases with increasing ionic strength, as observed by the same authors in earlier work on haemoglobin and serum albumin.<sup>3</sup> The changes are smaller in the case of egg albumin.

From the valence values thus obtained it is possible to calculate for each ionic strength an "ideal mobility"  $u_i$  according to the equation

$$u_i = \frac{F \times Z_p \times 3 \times 10^9}{f \times 3 \times 10^2} \text{ cm.}^2 \text{ volt.}^{-1} \text{ sec.}^{-1} \quad (1)$$

where  $F$  is the Faraday constant,  $Z_p$  the valence of the protein ion, and  $f$  the molar frictional coefficient in c.g.s. units, as obtained from the diffusion constant  $D$ . From Lamm and Polson's value,  $D_{20} = 7.76 \times 10^{-7}$ , we obtain  $f_{20} = 3.14 \times 10^{18}$  c.g.s., reduced to zero by the viscosity correction  $f_0 = 5.52 \times 10^{18}$  c.g.s. The mobilities thus obtained have been plotted in the diagram, Fig. 1 (upper curve). It is seen that the "ideal" and the observed mobilities approach each other at low ionic strengths, and the values extrapolated to  $I = 0$  are almost identical. At zero ionic strength, therefore, the egg albumin molecule actually migrates as a free ion.

The observed mobilities in the range of ionic strengths studied, are, however, considerably smaller than the ideal values, an effect which can be attributed mainly to the reduction of the electrokinetic potential caused by the double layer around the particle. This effect has been discussed mathematically by a number of different authors (for recent summaries see Kemp,<sup>12</sup> Moyer,<sup>13</sup> and Abramson, Gorin and Moyer.<sup>14</sup>

<sup>5</sup> Lamm and Polson, and Pedersen, quoted by Svedberg, *Proc. Roy. Soc., B*, 1939, 127, 1.

<sup>8</sup> Adair, *Annual Review of Biochemistry*, 1937, Vol. VI, 163.

<sup>10</sup> Adair, *Proc. Roy. Soc., B*, 1939, 127, 18.

<sup>11</sup> Kekwick and Cannan, *Biochem. J.*, 1936, 30, 227.

<sup>12</sup> *Trans. Faraday Soc.*, 1935, 31, 1347.

<sup>13</sup> *Cold Spring Harbor Symposia on Quantitative Biology*, 1938, VI, 228

<sup>14</sup> *Chemical Reviews*, 1939, 24, 345.

According to the theory of Debye and Hückel<sup>15</sup> the electrophoretic velocity of a charged spherical particle should be given by the expression

$$u = \frac{Z}{6\pi\eta r(1 + \kappa r)} \quad (2)$$

According to Stokes's Law  $u_i = \frac{Z}{6\pi\eta r}$  and therefore

$$\frac{u}{u_i} = \frac{1}{1 + \kappa r} \quad (3)$$

Henry<sup>16</sup> introduced an important modification in this theory, leading to the formula

$$u = \frac{Z}{4\pi\eta r(1 + \kappa r)} f(\kappa r) \quad (4)$$

where  $f(\kappa r)$  is a function which can be calculated from curves given by Henry. We have used Henry's equation for the calculation of the lower curve in the diagram, Fig. 1. The difference in the result when using (2) instead of (3) is only from 2 per cent. to 11 per cent., depending upon the ionic strength. As Henry emphasises himself, this treatment does not take the possible influence of the relaxation forces into account. There does not yet seem to be any satisfactory theoretical treatment of this effect, and it is quite possible that it can be neglected. In any case Fig. 1 shows clearly that in the system studied in the present investigation the experiments fit very well with the Debye-Hückel-Henry theory. In this connection mention should be made of the work of Abramson and Moyer (see ref. 14 above) who have studied extensively the relation between the migration velocity of protein-coated particles and the titration curves of the respective proteins. With certain assumptions their data fit well with the above-mentioned theory.

### Measurements in the Isoelectric Region.

In order to decide to what an extent the isoelectric point is dependent upon the ionic strength  $I$ , some experiments were made in the range of  $pH = 4.4-4.8$  and  $I = 0.10, 0.05, 0.02$  and  $0.01$  (acetate buffers). The position of the isoelectric point was obtained by straight line interpolation between two determinations at constant  $I$  but at different  $pH$  (Table II Fig. 2). Fig. 3 shows the isoelectric points thus determined as a function of the ionic strength.

TABLE II.—ISOELECTRIC POINT OF EGG ALBUMIN AT 0.5° IN ACETATE BUFFERS OF DIFFERENT IONIC STRENGTHS.

Ionic Strength $I$ .	$pH$	$u \times 10^5$ .	I.P.
0.10	4.560	+ 0.11	4.585
	4.745	- 0.75	
0.05	4.525	+ 0.55	4.630
	4.675	- 0.21	
0.02	4.605	+ 0.49	4.675
	4.685	- 0.07	
0.01	4.415	+ 2.18	4.710
	4.715	- 0.04	

very small mobilities in these experiments. Before closing the current the boundaries were brought out from behind the glass plates by the compensation arrangement described earlier,<sup>6</sup> so that they were visible

<sup>15</sup> *Physik. Z.*, 1923, 24, 185, 305, 334; 1924, 25, 97, 145.

<sup>16</sup> Henry, *Proc. Roy. Soc., A*, 1931, 133, 106.

from the start of the experiment. One could thus also make sure that no migration due to leakage took place.

The results show a marked dependence of the isoelectric point on the ionic strength, the former rising with falling salt concentration. A

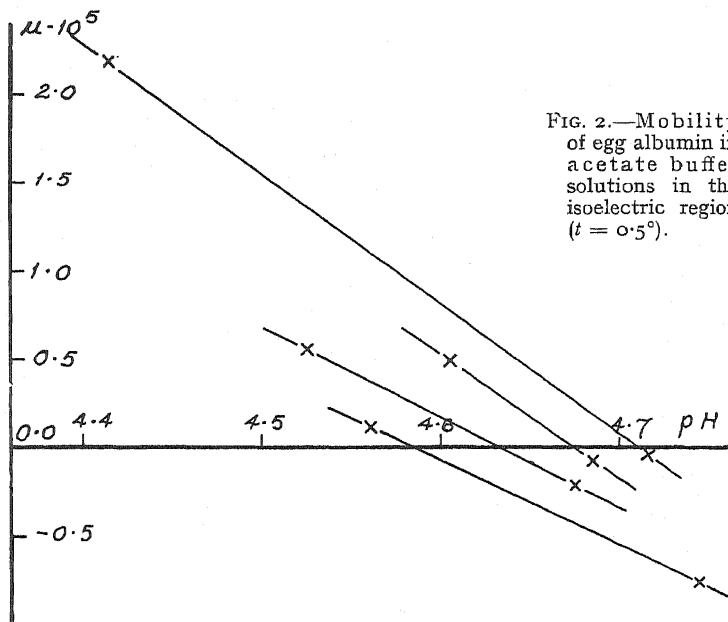


FIG. 2.—Mobility of egg albumin in acetate buffer solutions in the isoelectric region ( $t = 0.5^\circ$ ).

similar effect has been observed by Adair for hæmoglobin, both with membrane potential and electrophoresis methods.<sup>10</sup> The phenomenon may be explained by the assumption of a partial combination between the protein and the buffer ions, preferentially the anions. This would also,

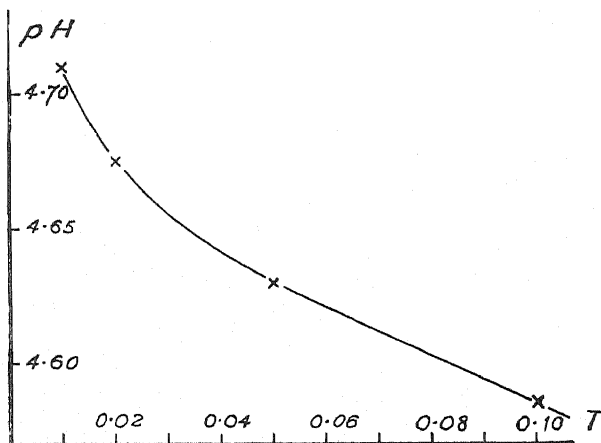


FIG. 3.—The isoelectric point of egg albumin in acetate buffer solutions as a function of the ionic strength ( $t = 0.5^\circ$ ).

partially at least, account for the difference in isoelectric and isoionic points for egg albumin, as has earlier been pointed out.<sup>3</sup> A preferential binding of negative ions by hæmoglobin in the isoelectric region has also been found by Adair and Adair<sup>2</sup> in their studies of membrane equilibria.



The results shown in Fig. 3 demonstrate that the isoelectric point approaches the isoionic point ( $pH$  4.86, see Sørensen, Linderström-Lang and Lund<sup>17</sup>) with falling salt concentration, although the difference even at  $I = 0.01$  is quite large. Unfortunately it is extremely difficult to extend the measurements to still lower salt concentrations to find out whether the two points at zero ionic strength would become identical or not.

The isoelectric point at  $I = 0.02$  has been determined earlier by one of the authors<sup>3</sup> and was found to be 4.55 at 20.0°. The value obtained above at 0.5° at the same ionic strength is higher (4.65), which indicates a marked dependence on the temperature. This was confirmed by measuring again, with the new apparatus, the isoelectric point at 20°, which was found to be 4.57 at  $I = 0.02$ .

As in the previous section  $pH$  values for mobilities at 0.5° refer to 0.5°. There is a difference of 0.025  $pH$  units between 0° and 20° for acetate buffers, as for acetic acid  $pH = 4.742$  at 0° and 4.717 at 20°, assuming the Sørensen value for the calomel cell.<sup>18</sup>

A similar variation with ionic strength of the isoelectric point of quartz particles coated with egg albumin has been found by Abramson<sup>19</sup> and studied especially by Smith.<sup>20</sup> We are not convinced, however, that the results of these authors are comparable with ours, as egg albumin seems to suffer some change in its electrochemical properties on adsorption. Thus the isoelectric point in 0.02 acetate buffer was found by Smith to be 4.82, whereas dissolved egg albumin at the same temperature, according to our measurements, gives the value 4.55-4.57.

### Summary.

The influence of salts upon the electrophoretic mobility and isoelectric point of egg albumin has been determined, using direct measurements, by the moving boundary method. As a limiting case at very low ionic strengths the protein migrates as a free ion. The reduction in mobility caused by increasing ionic strengths can be accounted for by the Debye-Hückel-Henry theory of electrophoresis.

The displacement of the isoelectric point by variation of the ionic strength has also been studied. It may be explained partially at least by the combination of other ions than H and OH with the protein.

We are much indebted to Dr. G. S. Adair, F.R.S., for valuable discussions of several questions of importance for this paper.

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<sup>17</sup> Sørensen, Linderström-Lang and Lund, *J. Gen. Physiol.*, 1926, 8, 585.

<sup>18</sup> Harned and Ehlers, *J. Am. Chem. Soc.*, 1932, 54, 1350.

<sup>19</sup> Abramson, *J. Gen. Physiol.*, 1933, 16, 593.

<sup>20</sup> Smith, *J. Biol. Chem.*, 1935, 108, 187.

# MEMBRANE POTENTIALS, VALENCES AND THEORETICAL AND OBSERVED MOBILITIES OF HÆMOGLOBIN AND EGG ALBUMIN.

BY G. S. ADAIR AND M. E. ADAIR.

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Mathematical relationships between the charges on surfaces and on colloidal particles and such electrokinetic properties as electro-osmosis and cataphoresis have been deduced by a number of workers, including Gouy,<sup>1</sup> Debye and Hückel,<sup>2</sup> Henry<sup>3</sup> and Abramson, Gorin and Moyer.<sup>4</sup> A review of the subject has been published by Kemp.<sup>5</sup>

Experimental investigations of the theories of cataphoresis have been carried out by Freundlich and Rona<sup>6</sup> and by Janssen,<sup>7</sup> who measured electrode potentials and stream potentials at glass surfaces, and by Abramson,<sup>8</sup> Kemp and Rideal<sup>9</sup> and Smith,<sup>10</sup> who studied the migration in an electrical field of microscopic particles coated with proteins. Such materials are well adapted for electrokinetic measurements, but thermodynamical investigations are limited to observations of hydrogen ion activities, and the effects of other ions must be deduced from the electrokinetic data, a circumstance which reduces the significance of comparisons between electrokinetic and thermodynamical measurements of potentials and charges, and it may be noted that the different authors have adopted entirely different methods of treatment of the thermodynamical data available.

The present communication records an investigation in which the same materials, with the same activities of electrolytes, have been used both for the thermodynamical determinations of potentials and charges and for electrokinetic measurements. The substances studied have been solutions of the proteins hæmoglobin and egg albumin, for which it is possible to obtain thermodynamic data concerning all of the ions and the non-electrolytes present in the system.<sup>11</sup>

The technique of Tiselius<sup>12</sup> for the measurement of the cataphoresis of proteins has been used for a series of determinations of the mobility of sheep hæmoglobin, a protein which has previously been subjected to detailed investigation by thermodynamic methods. Tiselius and

<sup>1</sup> Gouy, *J. Physique*, 1910, 9, 457.

<sup>2</sup> Debye and Hückel, *Physik. Z.*, 1924, 25, 49.

<sup>3</sup> Henry, *Proc. Roy. Soc., A*, 1931, 133, 105.

<sup>4</sup> Abramson, Gorin and Moyer, *Chem. Rev.*, 1939, 24, 345.

<sup>5</sup> Kemp, *Trans. Faraday Soc.*, 1935, 31, 1347.

<sup>6</sup> Freundlich and Rona, *Sitzb. Preuss. Akad. Wiss.*, 1920, 20, 397.

<sup>7</sup> Janssen, *Electrische Grensulak-Verschijnselen aan Glas*, Amsterdam, 1933.

<sup>8</sup> Abramson, *Electrokinetic Phenomena*, New York, 1934.

<sup>9</sup> Kemp and Rideal, *Proc. Roy. Soc., A*, 1934, 147, 11.

<sup>10</sup> Smith, *J. Biol. Chem.*, 1936, 113, 473.

<sup>11</sup> Adair, *Trans. Faraday Soc.*, 1937, 33, 1106, has given a list of papers describing thermodynamical methods for the study of protein systems.

<sup>12</sup> Tiselius, *Trans. Faraday Soc.*, 1937, 33, 524.

Svensson<sup>13</sup> have measured the mobility of egg albumin dissolved in phosphate and acetate buffers, and for comparison with their data, measurements of the thermodynamical properties of similar egg albumin solutions have been made, and are reported in this paper.

Dissolved proteins have certain disadvantages as materials for electrokinetic measurements. The range of salt concentrations which can be investigated is limited. A buffer solution not less concentrated than 0.01 M. is generally desirable to repress anomalies at the boundaries of protein solution and buffer, and to give well-defined *pH* values, while heat convection may be excessive if the salt concentration exceed 0.2 M.

### Methods.

Crystalline egg albumin was prepared and recrystallised three times as described by Taylor *et al.*<sup>14</sup> and dialysed against distilled water at 0.5° C. Carbon monoxide hæmoglobin was prepared from sheep's blood without crystallisation, as described by Adair and Adair.<sup>15</sup> The purified proteins were stored at -10° C.

The *pH* values were adjusted by dilution of the concentrated aqueous protein solutions with mixtures of acids, bases and salts, and the activities of the electrolytes were finally controlled by dialysis against relatively large volumes of standard buffer mixtures. The final *pH* values of the dialysates were measured in all cases with the hydrogen electrode. Calomel cells were standardised by assuming the *pH* value of 0.01 M. HCl + 0.09 M. KCl to be 2.04 at all temperatures and the liquid junction potentials with saturated KCl to be zero. Some of the *pH* determinations were made at the Low Temperature Research Station, Cambridge, at 1.5° C. At Upsala, the determinations were made at 19° C. and the values for 0.5° C. were calculated by adding + 0.10 units in the case of phosphate buffers, + 0.025 in the case of acetates and + 0.29 in the case of carbonates.

Measurements of the mobility of CO hæmoglobin were made at 0.5° C. as described by Tiselius,<sup>12</sup> using the "Schlieren" method for observation of the moving boundary. The concentrations of the protein solutions used varied from 0.2 to 0.5 per cent. Determinations of osmotic pressures, membrane potentials, refractive indices, densities and the concentrations of protein, sodium, phosphates and carbonates and calculations of thermodynamical properties based on these measurements have been described elsewhere.<sup>15</sup>

### Thermodynamical Investigations with Egg Albumin.

Tables I, II and III give the experimental results obtained when a series of collodion membranes containing egg albumin were in equilibrium with sodium phosphate buffer mixtures.

The final values for concentrations in g. mol. per litre of dialysate (measured at 18° C.) are recorded in Table I. The fourth column gives the CO<sub>2</sub> content before equilibration with hydrogen. The fifth column gives the CO<sub>2</sub> content of the dialysate in equilibrium with the hydrogen electrode. The *pH* values in the sixth column are not corrected for alterations in the CO<sub>2</sub> content; the corrections do not exceed 0.015 *pH* units. For the purpose of subsequent calculations, most of the numbers in Tables I, II and III include one more digit than is warranted by the absolute accuracy of the measurements.

Table II includes measurements on a series of relatively dilute protein solutions, in equilibrium with the fluids listed in Table I. The protein

<sup>13</sup> Tiselius and Svensson, *This Journal*, 16.

<sup>14</sup> Taylor, Adair and Adair, *J. Hygiene*, 1932, 32, 340.

<sup>15</sup> Adair and Adair, *Biochem. J.*, 1934, 28, 1230.

TABLE I.—ANALYSIS OF DIALYSATES.

Fluid No.	Molarity Na.	Molarity Total PO <sub>4</sub> .	Molarity CO <sub>2</sub> .	Molarity CO <sub>2</sub> after H <sub>2</sub> .	pH. 15° C.	Ionic Strength.
1	0.00749	0.00489	0.00017	0.00019	7.119	0.00992
2	0.00718	0.00403	0.00014	0.00011	7.576	0.01005
3	0.01491	0.01010	0.00023	0.00021	7.071	0.01949
4	0.01392	0.00813	0.00015	0.00015	7.532	0.01966
5	0.03700	0.02470	0.00022	0.00024	7.014	0.04908
6	0.03517	0.02039	0.00014	0.00020	7.480	0.04983
7	0.15050	0.09960	0.00033	0.00023	6.840	0.20107
8	0.14120	0.08130	0.00027	0.00035	7.343	0.20080

concentration  $C$  has been calculated by formula (1), in which  $n'$  represents the refractive index of the protein solution and  $n''$  that of the dialysate.

$$C = (n' - n'') (1/\alpha) \quad (1)$$

$C$  = g. anhydrous protein per 100 ml. solution at 18° C.;  $\alpha$  = the specific refraction increment, which is 0.001824 for egg albumin and 0.001945 for hæmoglobin.

The third column in Table II gives the osmotic pressure,  $p$ , in mm. Hg at 0.5° C. The fourth column gives the membrane potential,  $E$ , in millivolts at 0.5° C.; a negative sign indicates that the protein solution was negative.

TABLE II.—PROTEIN CONCENTRATIONS, OSMOTIC PRESSURES AND MEMBRANE POTENTIALS OF DILUTE SOLUTIONS OF EGG ALBUMIN.

Expt. No.	$C$ , g. protein/100 ml.	$p$ , mm. Hg at 0.5° C.	$E$ millivolts at 0.5° C.
1A	0.994	5.76	-3.29
2A	0.985	5.82	-3.39
3A	0.849	—	-1.46
4A	0.835	—	-1.45
5A	1.992	9.43	-1.42
6A	1.965	9.54	-1.55
7A	2.920	13.10	-0.57
8A	2.797	12.63	-0.61

Table III gives the osmotic pressures and the composition of a series of relatively concentrated protein solutions, numbered 1B to 8B, which were in equilibrium with the dialysates numbered 1 to 8 in Table I. The third column gives the total

TABLE III.—ANALYSES, OSMOTIC PRESSURES AND MEMBRANE POTENTIALS OF MORE CONCENTRATED EGG ALBUMIN SOLUTIONS.

Expt. No.	Molarity Na.	Molarity Total PO <sub>4</sub> .	$C$ .	$p$ .	$E$ .
1B	0.01129	0.00304	2.476	24.28	-8.34
2B	0.01150	0.00216	2.497	26.78	-9.12
3B	0.02240	0.00600	4.967	52.30	-8.52
4B	0.02192	0.00423	4.968	58.10	-9.58
5B	0.04343	0.01996	4.947	33.00	-3.52
6B	0.04130	0.01518	4.967	35.85	-3.88
7B	0.15200	0.09210	4.873	24.65	-0.98
8B	0.14340	0.07340	4.970	25.70	-1.07

phosphate. Methods for the calculation of the proportions of the univalent and bivalent ions  $H_2PO_4$  and  $HPO_4$  have been discussed elsewhere.<sup>15</sup>

It is possible to calculate the "corrected concentrations," expressed

in g. mol. per litre of solvent, from the measurements recorded in Tables I, II and III, by means of formulæ 2 and 3.

$$[\text{Na}]_c = [\text{Na}]' (100/100 - vC) \quad (2)$$

$[\text{Na}]_c$  = corrected concentration of sodium ions.  $[\text{Na}]'$  = observed concentration.  $v$  = volume occupied by 1 g. dry protein. The partial specific volume of egg albumin, calculated from density measurements, was found to be 0.7328 at 1.0° C. and this value was used to calculate minimum values for  $[\text{Na}]_c$ . Determinations<sup>18</sup> of the densities of egg albumin crystals indicate that in highly concentrated sodium phosphate buffers, 0.32 g. water may combine with 1 g. protein. It is possible that the hydration is slightly greater in dilute solutions, but the total correction for hydration cannot increase  $[\text{Na}]_c$  by much more than 2 per cent. in the solutions used in this work. In the case of hæmoglobin, a value<sup>15</sup> of 0.965 was used for  $v$ .

The corrected concentration of the protein  $[\text{Pr}]_c$ , and also the corrected percentage concentration  $C_v$ , expressed in g. per 100 ml. of solvent were calculated by formula 3.

$$[\text{Pr}]_c = (10C/M) (100/100 - vC) = 10C_v/M \quad (3)$$

$M$  = molecular weight. The value adopted for hæmoglobin is 67,000. For egg albumin, a revised value of 45,000 was adopted, after discussion with Professor Tiselius, as a mean of the values 46,000, deduced from recent measurements of osmotic pressure<sup>14</sup> and 44,000, deduced from measurements of diffusion, made by Lamm and Polson and of sedimentation velocity, made by Pedersen, which have not yet been published in detail.<sup>17</sup>

The minimum molecular weight of the hydrated egg albumin is 59,600, and the density is 1.239 in the crystalline form, and therefore the molar volume  $V_s$  is 48,200 ml. The radius of the molecule, calculated by the formula  $r = 0.34025(V_s/100,000)^{1/3} \times 10^{-8}$  is  $26.7 \times 10^{-8}$  cm. The maximum value for the radius calculated from measurements of diffusion is  $27.5 \times 10^{-8}$  cm. The agreement between minimal and maximal estimations of the radius indicates that the molecule is nearly spherical.<sup>18</sup> The surface area of a sphere of radius  $27.5 \times 10^{-8}$  cm. is 9500 Å., and for certain purposes it may be assumed that the surface area of the molecule is of the same order of magnitude.

In solutions of proteins that are not too dilute, the total surface area of the molecule in 1 ml. is so great that it is possible to measure the surface excess of ions by electrometric and chemical methods. Values for the excess of sodium ions, defined by formulæ 4 and 5, are given in Table IV. Similar formulæ were used for the calculations of the excess of phosphate ions.

TABLE IV.—IDEAL AND OBSERVED CONCENTRATIONS OF IONS.

Expt. No.	$[\text{Na}]_i$	$[\text{Na}]_c$	$b_{\text{Na}}$	$[\text{PO}_4]_i$	$[\text{PO}_4]_c$	$b_{\text{PO}_4}$
1B	0.0107	0.0115	1.4	0.0029	0.0031	0.4
2B	0.0106	0.0117	1.9	0.0021	0.0022	0.2
3B	0.0214	0.0232	1.6	0.0060	0.0062	0.2
4B	0.0209	0.0227	1.6	0.0041	0.0044	0.2
5B	0.0429	0.0451	1.4	0.0198	0.0207	0.8
6B	0.0415	0.0429	1.2	0.0154	0.0158	0.3
7B	0.1570	0.1576	0.5	0.0936	0.0956	1.7
8B	0.1476	0.1488	1.0	0.0750	0.0762	1.0

<sup>18</sup> Adair and Adair, *Proc. Roy. Soc., B*, 1936, 120, 422.

<sup>17</sup> Quoted by Svedberg, *ibid.*, 1939, 127, 1.

<sup>18</sup> Adair, *ibid.*, 18.

$$[\text{Na}]_i = [\text{Na}]'' (\text{antilog} - z_i EF / 2.303 \cdot 1000 RT) \quad (4)$$

$[\text{Na}]_i$  = the ideal value of the corrected concentration of sodium ions in the protein solution;  $[\text{Na}]''$  = the concentration in the dialysate;  $z_i$  = the valence of the sodium ion.

$$b_{\text{Na}} = b_c + b_a + b^* = ([\text{Na}]_c - [\text{Na}]_i) / [\text{Pr}]_c \quad (5)$$

$b_{\text{Na}}$  = the excess of ions in mols. per mol. of protein. The term  $b_{\text{Na}}$  can be regarded as the sum of three terms, namely  $b_c$ , the number of ions fixed on or within the surface of the protein;  $b_a$ , the excess of ions in the diffuse layer surrounding the molecule, attracted by forces of the type described by Debye and Hückel, and  $b^*$ , which is a correction term, representing such factors as hydration, inequalities of the liquid junction potential and differences of hydrostatic pressure.

Including the corrections for hydration referred to above, the values for  $b_{\text{Na}}$  are increased to 2.0 in the more dilute solutions and to 3.5 in the more concentrated solutions. These values are small, in relation to the surface area of the protein molecule. A similar area at the air-water interface can adsorb about 500 molecules of a fatty acid.

It is remarkable that the values of  $b_{\text{PO}_4}$  are so small. Low values for  $b_{\text{PO}_4}$  seem to be a characteristic of egg albumin at  $pH$  values above 6.8. Determinations of isoelectric points<sup>20</sup> show that this protein should have an affinity for anions, including acetates, at  $pH$  values below 5. Serum albumin<sup>21</sup> and hæmoglobin<sup>15</sup> may have values for  $b_{\text{PO}_4}$  of 4 or more at  $pH$  7. In the case of egg albumin, where the values of  $b_{\text{PO}_4}$  are low, the conditions are favourable for systematic investigations of the valence of the protein ions.

The mean electric charge or mean valence of the protein ions can be defined by formula 6.

$$z_p [\text{Pr}]_c = [\text{Free Anions}]_c - [\text{Free Cations}]_c \quad (6)$$

where  $z_p$  denotes the mean valence, which is negative for sodium proteinates.  $[\text{Free Anions}]_c$  denotes the sum of equivalent concentrations of diffusible anions, present in the free state uncombined with the protein, and expressed in gram equivalents per litre of solvent.

In order to evaluate the true concentrations of free ions, thermodynamical formulæ must be used in conjunction with approximate theoretical assumptions concerning the properties of inorganic ions in protein solutions. Estimations of the valence from titration curves, for example, may be inaccurate if any ions with the exception of H and OH can combine with the protein.<sup>8</sup>

A number of methods for the estimation of the valence of protein ions have been discussed in a previous communication,<sup>18</sup> in which the term "apparent valence" was applied to values calculated with the aid of simplifying assumptions. A modified notation is suggested in Table V, in which the ratio  $z_p/\alpha_z$  denotes an apparent valence deduced from chemical analyses, the product  $z_p g_z$  an apparent valence deduced from the osmotic pressures and  $z_p f_z$  an apparent valence deduced from membrane potentials. The symbols  $\alpha_z$ ,  $g_z$ , and  $f_z$  represent functions defined by formulæ 7, 8 and 9, which can be regarded as modified types of ionisation, osmotic and activity coefficients.

$$z_p = b_H \alpha_z \quad (7)$$

$\alpha_z$  = a modified ionisation coefficient, equal to unity in a system where sodium albuminate containing  $-b_H$  mols. of sodium per mol. of protein is fully dissociated, and where no phosphates or other ions which may be present in the solution, with the exception of H and OH, combine with the protein. The term  $-b_H$  in Table V, column 3, represents the NaOH

<sup>19</sup> Adair and Adair, *Trans. Faraday Soc.*, 1935, **31**, 130.

<sup>20</sup> Tiselius, *Nova Acta Reg. Sci. Upsala IV*, 1930, **4**, 7.

<sup>21</sup> Adair and Adair, *Comptes Rend. lab. Carlsberg*, 1938, **22**, 8.

combined in the presence of phosphate buffers, estimated from the analytical data for sodium and phosphates and the membrane potentials recorded in Tables I and III, as described by Adair and Adair.<sup>15</sup> This method is more laborious than the usual method of estimating the base combined from titration curves, but it simplifies the theoretical treatment by eliminating corrections for the effects of salts, discussed by Kemp and Rideal.<sup>9</sup>

TABLE V.—VALENCE OF EGG ALBUMIN IONS.\*

Ionic Strength.	pH Dialysate.	$-z_p/\alpha_z$ or $-b_H$	$-z_p g_z$	$-z_p f_z$ Conc.	$-z_p f_z$ Dilute.	$-z_p f_z$ Very Dilute.
0.01	7.12	12.5	10	11.4	11.9	12.0
0.01	7.58	14.1	11	12.2	12.4	12.4
0.02	7.07	11.9	10	11.2	12.4	12.6
0.02	7.53	13.6	11	12.3	12.7	12.7
0.05	7.01	13.0	11	12.2	12.8	13.2
0.05	7.48	14.2	12	13.4	14.3	14.8
0.20	6.84	12.9	—	14.4	14.4	14.4
0.20	7.34	15.1	—	15.8	15.8	15.8

\* Sodium salts of egg albumin, in equilibrium with dialysates of ionic strengths and pH values given in columns 1 and 2. See also Table I. Columns 3, 4 and 5 give apparent valences of the relatively concentrated albumin solutions described in Table III. Column 6 refers to more dilute solutions described in Table II. Column 7 gives extrapolated values for 0.22 per cent. solutions.

The product  $z_p g_z$  in Table V, column 4, represents the apparent valence calculated from measurements of osmotic pressure in Table III and of ionic strength in Table I, by formula 8.

$$z_p g_z = (e_a/I)^{\frac{1}{2}} \cdot \phi_e \cdot 2I[\text{Pr}]_e. \quad (8)$$

$g_z$  = a modified type of osmotic coefficient;  $e_a$  = the apparent excess of diffusible ions inside the membrane, calculated by the formula  $e_a = \{p/RT\} - [\text{Pr}]_e$ . The symbol  $\phi_e$  represents a mathematical function calculated from (unpublished) tables of membrane equilibrium of ideal solutions of ions of different valences.  $I$  = the ionic strength.

The fifth column of Table V gives values for the "apparent" valence or the product  $z_p f_z$  defined by formula 9, calculated from the membrane potentials of relatively concentrated egg albumin solutions recorded in Table III.

$$z_p f_z = ([\text{Anions}]_i - [\text{Cations}]_i)/[\text{Pr}]_e. \quad (9)$$

$[\text{Anions}]_i$  = sum of the ideal values of the equivalent concentration of diffusible anions in the protein solution, calculated by formula 4,  $f_z$  = a modified type of activity coefficient, equal to unity in systems where the liquid junction potentials KCl/dialysate and KCl/protein are equal, and the activity coefficients of the free ions in the protein solution and the dialysate are equal. The term  $f_z$  may also be equal to unity in systems where the protein affects the activity coefficients of the free ions, if terms of the form  $b_a$  and  $b^*$  for anions and cations cancel out. (Formula 5.)

Additional measurements of  $-z_p f_z$  for the more dilute protein solutions described in Table II are recorded in Table V, column 6, and extrapolated values for a protein concentration of 0.22 per cent. are given in Table V, column 7. All values at an ionic strength of 0.2, where the membrane potentials are small, are based not on individual measurements but on an average value for the ratio  $E/C_v$ .

A number of conclusions can be drawn from the results summarised in Table V.

(1) The range of variation of  $z_p f_z$  with alterations in protein concentration is about 10 per cent., an unusually small variation.

(2) Apparent valences for the same solution calculated by different methods, namely  $z_p/\alpha_z$ ,  $z_p/g_z$  and  $z_p/f_z$ , although not identical, are more nearly equal than values for all other colloidal electrolytes for which comparable data are available, namely edestin, serum albumin, hæmoglobin and congo red. The values for  $-z_p g_z$  are rather less than either  $z_p/\alpha_z$  or  $z_p f_z$ , but this difference can be explained by the fact that the osmotic pressure is a function of the mean activities of sodium and protein ions.

(3) It seems probable that the degree of dissociation of the sodium proteinate is nearly complete, and that the coefficient  $f_z$  is almost unity at low protein concentrations.

### The Valence of Hæmoglobin in Buffer Mixtures.

Previous investigations<sup>15</sup> have shown that at  $pH$  values below 8, hæmoglobin may combine with or attract chloride and phosphate ions, and that the apparent valence  $z_p/\alpha_z$  deduced from chemical analyses is more positive than  $z_p f_z$  deduced from membrane potentials. It is probable that  $z_p f_z$  is a better approximation to the true valence than  $z_p/\alpha_z$ , and all values recorded in Table VI have been calculated from membrane

TABLE VI.—VALENCE OF CARBON MONOXIDE HÆMOGLOBIN.

Buffers.	Ionic Strength 0.02.		Ionic Strength 0.10.	
	$pH$ .	$z_p f_z$ .	$pH$ .	$z_p f_z$ .
$Na_2HPO_4$ , $NaH_2PO_4$	6.28	+ 2.2	6.03	+ 0.3
" "	6.77	+ 1.0	6.60	- 1.9
" "	7.46	- 1.6	7.41	- 4.0
" "	7.79	- 2.9	8.04	- 6.4
$Na_2CO_3$ , $NaHCO_3$	10.09	- 11.3	9.11	- 12.7
" "	—	—	9.95	- 16.4

potentials of the preparations of sheep hæmoglobin used in this work. In order to facilitate the calculations in cases where the potentials are small, formula 10 was derived from formula 9.

$$z_p f_z = [F/5000RT] \phi_z MI(E/C_v) \quad . \quad . \quad . \quad (10)$$

The factor  $[F/5000RT] = 0.0084835$  at  $0.5^\circ C$ . The symbol  $\phi_z$  represents a mathematical function equal to unity when  $E$ , the membrane potential (in millivolts), is small. Values of  $\phi_z$  can be calculated by applying formulæ 9 and 10 to ideal systems. These values range from 0.985 at a potential of - 1 millivolt to 0.938 at a potential of - 5 millivolts, if the buffers contain equal amounts of  $Na_2HPO_4$  and  $NaH_2PO_4$ .  $I$  = the ionic strength of the buffer solution;  $M$  = the molecular weight. It has been shown<sup>21</sup> that osmotic pressures of hæmoglobin in buffer mixtures are consistent with a constant value of 67,000 for the molecular weight over the range from  $pH$  6 to  $pH$  11.

It has been observed<sup>22</sup> that the ratio  $E/C_v$  is practically constant when  $E$  is less than 1.5 millivolts, and the product  $z_p f_z$  is then equal to  $568 I(E/C_v)$ .



In Fig. 1 theoretical mobilities of hæmoglobin ions, calculated from measurements of the valence given in Table VI, are represented by the continuous lines marked 2 and 4, and the observed mobilities are represented

by the interrupted lines 1 and 3. The preparations of hæmoglobin and the buffers used for the direct measurements of mobilities, by the method of Tiselius,<sup>12</sup> were the same as those used for the determinations of membrane potentials and valences, listed in Table VI.

Over the greater part of the range investigated, the agreement between the observed and the theoretical mobilities shown in Fig. 1 is closer than might have been anticipated, in view of the simplifying assumptions which have been made in the theory, and it seems that in certain cases, the empirical corrections suggested by Abramson,<sup>8</sup> may be unnecessary, when the charge is calculated from membrane potentials rather than titration curves.

The differences between the theoretical and the observed mobilities are greater at the lower  $pH$  values, in the region of the iso-electric point.

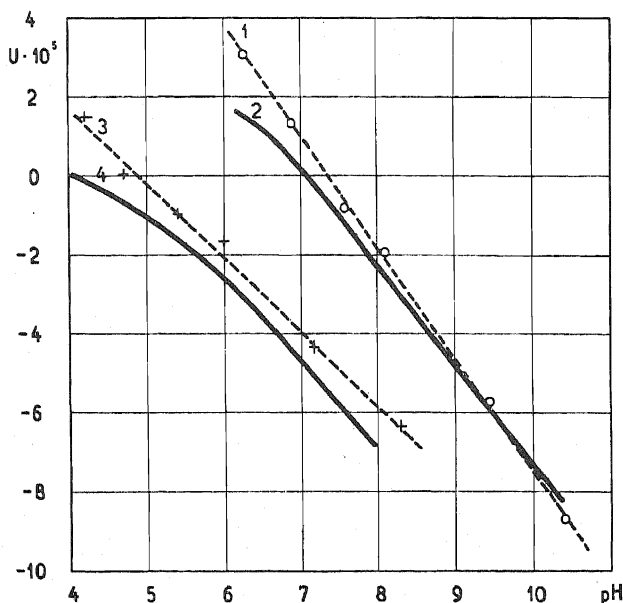


FIG. 1.—Comparison of observed and theoretical mobilities of hæmoglobin ions. Ordinates, mobilities  $\times 10^5$ ; abscissæ,  $pH$  value. Curve 1 and circles observed mobility, ionic strength 0.02,  $u_i = 0$  at  $pH$  7.3. Curve 2 theoretical mobility, ionic strength 0.02,  $u_i = 0$  and  $E = 0$ ,  $pH$  7.05. Curve 3 and crosses observed mobility, ionic strength 0.10,  $u_i = 0$  at  $pH$  6.8. Curve 4 theoretical mobility, ionic strength 0.10,  $u_i = 0$  at  $pH$  6.1. Curves 3 and 4 are shifted two  $pH$  units to the left.

Further investigations are required, with special reference to the stability of hæmoglobin at  $pH$  values below 7, in order to account for these differences and to determine the iso-electric points with precision.

Preliminary values for the apparent iso-electric points are shown in Fig. 1. Earlier measurements of the cataphoresis of hæmoglobin made by Michaelis<sup>23</sup> failed to show any effects of salts on the iso-electric point. Determinations made by the method of Tiselius and by membrane potentials agree in that values for the apparent iso-electric point are below the iso-ionic point ( $pH$  7.5) and are diminished by an increase in salt concentration. Lower values are deduced from membrane potential measurements than from cataphoresis, a difference which might be accounted for by inhomogeneity of the protein or by liquid junction potentials.

<sup>23</sup> Michaelis and Davidsohn, *Biochem. Z.*, 1912, 41, 102.

In the case of egg albumin, the  $pH$  values at which  $E = 0$  was found to be 4.625 in acetate buffers of ionic strength 0.02, a fairly close agreement with the value of 4.65 found by Tiselius and Svensson.<sup>13</sup>

### Summary.

The membrane potentials, the valences and the excess of inorganic ions in the neighbourhood of a protein ion have been investigated for comparison with measurements of the cataphoresis of dissolved proteins.

Calculations of the mobilities of the ions of hæmoglobin, based on measurements of the charge and radius, using Henry's formula, are in fairly close agreement with the observed mobilities.

We wish to thank Professor Svedberg for the privilege of working in his Institute and Professor Tiselius for his advice and assistance.

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## THE INFLUENCE OF ELECTROLYTES ON THE ELECTROPHORETIC MOBILITY OF SERUM ALBUMIN AND HÆMOCYANIN.

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### 1.\*

The electrophoretic mobility of an insulating particle whose radius of curvature is large compared with the effective thickness of the electrical double layer, is independent of the size of the particle and obeys the law of Smoluchowski:

$$v = \frac{D\xi}{4\pi\eta} \quad \dots \quad (1)$$

According to D. C. Henry<sup>1</sup> this equation is valid for particles whose radius is not less than 300 times the thickness of the double layer ( $\kappa a > 300$ ); for smaller particles the mobility varies with size and departs more and more from equation 1, until, for very small particles,

#### \* Symbols and Constants :

- $v$  electrophoretic mobility in E.S.U.
- $U$  electrophoretic mobility in cm. Volt<sup>-1</sup> sec.<sup>-1</sup>;  $v = 300 U$ .
- $D$  dielectric constant; at 25°  $D = 78.8$ .
- $\eta$  coefficient of viscosity; at 25°  $\eta = 0.00894$
- $e$  charge of electron =  $4.774 \times 10^{-10}$  E.S.U.
- $h$  Boltzmann's constant  $1.37 \times 10^{-16}$ .
- $a$  radius of particle.
- $\kappa$  reciprocal of the effective thickness of the electric double layer;  
 $\kappa = 3.279 \times 10^7 \sqrt{\mu}$  at 25°.
- $\mu$  ionic strength.

<sup>1</sup> D. C. Henry, *Proc. Roy. Soc., A*, 1931, 133, 106.

whose radius is about 0.5 the thickness of the double layer ( $\kappa a \leq 0.5$ ), the equation of Hückel becomes valid :

$$v = \frac{D\zeta}{6\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

There is thus a region of dimensions where the electrophoretic mobility is governed by laws intermediate between the two extremes represented by the equations of Smoluchowski and Hückel. The molecular dimensions of the proteins place them on the lower boundary of this intermediate region ; from this point of view the study of their mobility is particularly interesting. The experiments here reported were performed with two proteins serum albumin (horse) having a low molecular weight and a small radius ( $a = 2.74 \times 10^{-7}$ ), the other, Hæmocyanin (*Helix pomatia*) having a very high molecular weight and a large radius ( $a = 1.25 \times 10^{-6}$ ). For ionic strengths of 0.01 to 0.1 their  $\kappa a$  values range from 0.9 to 2.8 for serum albumin and from 4.1 to 13 for hæmocyanin. The potential  $\zeta$  is related to the charge of the particle by the equation :

$$\zeta = \frac{n\epsilon}{Da(1 + \kappa a)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the case of an ampholyte ion, having a large number ( $2q$ ) of ionisable acid and basic groups, Linderström-Lang<sup>2</sup> has derived an equation relating the average number of charges  $n$  to the acidity of the solution :

$$n = \frac{p_{H_0} - p_H}{0.8686 \left( w + \frac{1}{q} \right)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where 
$$w = \frac{\epsilon^2}{2DkTa(1 + \kappa a)},$$

$p_{H_0}$  being the isoelectric point.

Equation 4 is valid if no other ions than hydrogen ions combine with or are given off by, the ampholyte ion.

Combining (3) and (4) with either (1) or (2), the following two equations obtain :

$$U = \frac{1.63 \times 10^{-11}}{3.53 \times 10^{-8} + \frac{a(1 + \kappa a)}{q}} (p_{H_0} - p_H) \quad . \quad . \quad . \quad (5)$$

$$U = \frac{1.087 \times 10^{-11}}{3.53 \times 10^{-8} + \frac{a(1 + \kappa a)}{q}} (p_{H_0} - p_H) \quad . \quad . \quad . \quad (6)$$

These equations correlate the electrophoretic mobility of a macro-ampholyte ion with the variation of acidity and the ionic strength of the solution, as a first approximation only.<sup>1,2</sup> Ion association or specific interaction have not been taken into account in their derivation ; but they are useful as a guide in the interpretation of experimental results.

## 2.

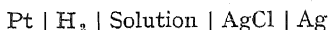
We have used the moving boundary method of Tiselius, in its original form, using light absorption in the short-wave ultraviolet. The technique has been fully described by A. Tiselius<sup>3</sup> and K. O. Pedersen.<sup>4</sup>

<sup>2</sup> K. Linderström-Lang, *Compt. rend. Carlsberg*, 1924, 15, no. 7.

<sup>3</sup> A. Tiselius, *Nova Acta Reg. Soc. Scient. Upsala*, 1930, IV, 7, no. 4.

<sup>4</sup> K. O. Pedersen, *Kolloid Z.*, 1933, 63, 258.

A departure from the current procedure was made with respect to the measurement of the acidity of the solutions, since  $pH$  measurements are affected by an experimental uncertainty due to the diffusion potential. As appears from (5) and (6), only the difference between two  $pH$  values is of importance; if the diffusion potential is different in both measurements, cancellation does not occur and may introduce an error, affecting more particularly the shift of the isoelectric point. If, however, as proposed by D. I. Hitchcock,<sup>5</sup> a cell of the type



is used, provided the solution contains a known concentration of chloride ions, a measure ( $H$ ) of the acidity of the solution\* is obtained from the electromotive force of the cell:

$$H = -\log a_{\text{H}_3\text{O}^+} = 16.91 (E - E_0) - \frac{1}{2}p_{\text{H}_2} + \log C_{\text{Cl}^-}$$

This equation is valid at  $25^\circ$ ;  $E_0 = 0.2224$ .

It is easily seen that for two solutions of the same ionic strength, the difference between the two "acidity functions"  $H$  is equal to the difference of two ideal  $pH$  values, unaffected by diffusion potentials. This remains true even if the chloride ion concentration is altered by chemical combination with the protein, provided the combined amount is the same in both cases. To conform with the requirement of a known concentration of chloride ions the solutions were always made up to contain 0.01 equivalents of chloride ions per litre of solution.

They further contain the required amount of acetate to bring the solution to the given ionic strength and the concentration of acetic acid corresponding to the given acidity. With respect to the anions the solutions were henceforth mixtures of acetate and chloride, but they always contained cations of only one kind.

### 3.

If the results given in Tables I to IV are put in a diagram relating the mobility to the acidity of the solution, it appears that the linearity required by equation 5 or 6 is satisfactorily realised on the acid side (cathodic migration) of the isoelectric point, but that on the alkaline side the bending of the curves is strongly marked.

Considering first the cathodic migration, we have calculated the slope  $\Delta U/\Delta H$  of the lines by taking the average of the slopes given by all the possible pairs of results. Knowing the slope, and taking the  $H_c$  and  $U_c$  values of the centre of gravity of the curve, it is easy to calculate the  $H_0$  value corresponding to the isoelectric point:

$$H_0 = H_c + \frac{U_c}{\Delta U/\Delta H} \quad (7)$$

The values of the slopes and the  $H_0$  values are given in the tables.

For a solvent of the same composition (Tables I and III), but with ionic strength varying from 0.02 to 0.06, the isoelectric point of hæmocyanin is very nearly constant; the isoelectric point of serum albumin appears to undergo a shift of 0.04 units towards the alkaline side, for an increase of ionic strength from 0.03 to 0.06. The results are too erratic to justify calculation for 0.02 in the case of serum albumin.

At constant ionic strength (Tables II and IV), but with a variety of divalent cations the isoelectric point of hæmocyanin is shifted from 5.06

<sup>5</sup> D. I. Hitchcock, *J. Am. Chem. Soc.*, 1936, 58, 855.

\*  $C_{\text{Cl}^-}$  = concentration of chloride ion in moles per litre of solution.

$p_{\text{H}_2}$  = pressure of dry hydrogen in atmospheres.

(for Na and Li) to a value 0.15 to 0.22 units higher, agreeing with the shift for serum albumin (0.15 to 0.20). These results do not show the regularities found by E. R. B. Smith<sup>6</sup> for the isoelectric point of ovalbumin.

TABLE I.—HÆMOCYANIN  $t^{\circ} 25^{\circ}$ .

Concentration of protein, 0.1 per cent.; sodium chloride, 0.01 M.; sodium acetate 0.01, 0.02 or 0.03 M. according to ionic strength.  
 $U$  in cm./volt, sec.  $\times 10^5$ .

	$\mu = 0.02$		$\mu = 0.03$		$\mu = 0.06$	
	$H$ .	$U \times 10^5$ .	$H$ .	$U \times 10^5$ .	$H$ .	$U \times 10^5$ .
Migration cathodic.	4.54	7.1	4.10	9.8	4.48	3.9
	4.70	4.4	4.38	7.5	4.62	3.3
	4.77	4.0	4.77	2.8	4.78	1.8
	4.88	2.4	5.06	0.7	—	—
Slope	13.9		10.24		6.9	
$H_0$	5.05	0.0	5.06	0.0	5.07	0.0
Migration anodic.	5.80	4.6	5.47	2.7	5.48	2.3
	6.56	7.5	5.77	4.1	5.78	3.5
	—	—	6.37	6.6	5.98	4.4
	—	—	6.40	6.9	6.19	4.8

TABLE II.—HÆMOCYANIN  $t^{\circ} 25^{\circ}$ .

Concentration of protein, 0.1 per cent.; Concentration of chloride ion, 0.01; constant ionic strength equal to 0.03; acetate buffers.  
 $U$  in cm./volt, sec.  $\times 10^5$ .

	Li.		Mg.		Ca.		Ba.	
	$H$ .	$U \times 10^5$ .	$H$ .	$U \times 10^5$ .	$H$ .	$U \times 10^5$ .	$H$ .	$U \times 10^5$ .
Migration cathodic	4.42	6.0	4.47	7.1	4.44	8.1	4.49	7.1
	4.68	3.8	4.76	4.1	4.74	5.2	4.63	6.1
	4.77	2.8	4.90	3.0	4.97	2.9	4.79	4.0
	—	—	—	—	—	—	5.00	2.0
Slope	10.12		9.24		9.83		10.20	
$H_0$ .	5.05	0.0	5.22	0.0	5.27	0.0	5.20	0.0
Migration anodic	5.30	1.2	5.46	0.6	5.42	0.6	5.51	0.8
	5.59	3.2	5.74	1.9	5.75	1.6	5.83	1.7
	5.61	3.1	5.98	2.4	6.00	2.4	6.13	2.4
	6.14	5.6	—	—	—	—	—	—
	6.84	7.7	—	—	—	—	—	—

<sup>6</sup> E. R. B. Smith, *J. Biol. Chem.*, 1936, 113, 473.

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TABLE III.—SERUM ALBUMIN  $t^{\circ} 25^{\circ}$ .

Concentration of protein, 0.25 per cent.; sodium chloride, 0.01 M.;  
sodium acetate 0.01, 0.02 or 0.03 according to ionic strength.  
 $U$  in cm./volt, sec.  $\times 10^5$ .

	$\mu = 0.02$		$\mu = 0.03$		$\mu = 0.06$	
	$H.$	$U \times 10^5$	$H.$	$U \times 10^5$	$H.$	$U \times 10^5$
Migration cathodic.	4.32	10.0	4.29	9.7	4.15	9.9
	4.46	7.4	4.45	7.3	4.46	5.5
	4.73	4.4	4.75	2.4	4.75	2.7
	4.75	4.0	—	—	—	—
Slope	—		15.7		11.9	
$H_0$	—	—	4.91	0.0	4.95	0.0
Migration anodic	5.46	3.8	5.45	3.8	5.45	3.4
	5.74	5.9	5.75	6.2	5.73	5.2
	5.99	7.1	6.05	7.5	6.03	5.7
	—	—	—	—	—	—

TABLE IV.—SERUM ALBUMIN  $t^{\circ} 25^{\circ}$ .

Concentration of protein, 0.25 per cent.; concentration of chloride ion,  
0.01; constant ionic strength equal to 0.03; acetate buffers.  
 $U$  in cm./volt, sec.  $\times 10^5$ .

	Mg.		Ca.	
	$H.$	$U \times 10^5$	$H.$	$U \times 10^5$
Migration cathodic	4.25	12.1	4.23	13.1
	4.47	9.3	4.40	9.9
	4.75	5.1	4.70	5.9
	—	—	—	—
Slope.	13.9		15.8	
$H_0$	5.13	0.0	5.05	0.0
Migration anodic	5.72	1.9	5.40	0.8
	5.83	2.8	5.68	2.2
	—	—	5.89	2.9
	—	—	—	—

The shift of isoelectric point is without consequence for the application of equation 5 or 6, only the difference between the acidity functions appearing in the equation.

From the considerations underlying the derivation of these equations it is anticipated that the slopes of the curves should be the same at the same ionic strength, independent of the nature of the electrolytes present. Within the limits of experimental error this is realised for haemocyanin;

the insert of Fig. 1 shows that the line having the average slope of all the points at  $\mu = 0.03$  satisfactorily agrees with all the data. For

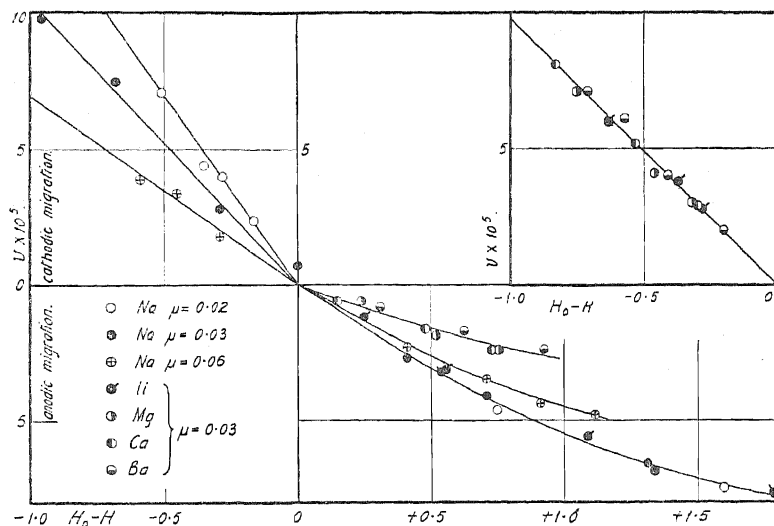


FIG. 1.—Electrophoretic mobility of haemocyanin at 25°. The insert at the upper right was drawn separately in order not to clog the part of the diagram showing the cathodic migration.

serum albumin the agreement is less good, only the points obtained with sodium and calcium admitting the same slope, the results obtained with magnesium salts being distinctly different (Fig. 2).

If the slope is constant for a series of data, then a constant value of the number of ionisable basic groups  $q$  will be found. The two equations 5 and 6 do not, however, give the same result. Thus, it is found that haemocyanin has 81 basic groups according to equation 5, but 142 according to equation 6. The corresponding values for serum albumin are 10 and 21 respectively (all values calculated with the slope at  $\mu = 0.03$ ). It should be possible to decide between the two alternatives by calculating the  $q$  values from titration data. See K. Linderström-Lang and Elen Lund.<sup>7</sup>

Once the number of ionisable groups is known at one ionic strength, it is possible to calculate the mobility at any one other ionic strength. The result is disappointing. Equations 5 and 6 give slightly different values for the slopes at  $\mu = 0.02$  and  $\mu = 0.06$  calculated from the values at  $\mu = 0.03$ , but both equations agree in

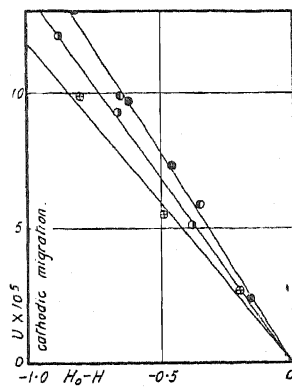


FIG. 2.—Cathodic migration of serum albumin at 25°.

The points are marked as in Fig. 1.

Upper curve: migration at 0.03 in presence of Na and Ca.

Middle curve: migration at 0.03 in presence of Mg.

Lower curve: migration at 0.06 in presence of Na.

<sup>7</sup> K. Linderström-Lang and E. Lund, *Compt. rend. Carlsberg*, 1926, 16, no. 5.



making the dependency on the ionic strength much smaller than is apparent from the experimental results.

The curves representing the anodic migration are still much less easy to interpret indicating the influence of factors neglected by the simple theory. One may of course expect much more influence of the cations on the protein anions than on the acid side of the isoelectric point where the protein is itself cation. That these more complicated relationships may perhaps find a simple solution at least as a first approximation, is indicated by the fact that at constant ionic strength and acidity the average mobility of the protein ions in presence of divalent cations is quite exactly half the mobility in presence of monovalent cations (see Fig. 1).

Attention may be called to the fact that, whereas our results for hemocyanin agree with those previously found by us<sup>8</sup> and by Tiselius,<sup>3</sup> our results for serum albumin are much higher than the published data. See Tiselius,<sup>3</sup> L. S. Moyer and H. A. Abramson,<sup>9</sup> R. A. Kekwick.<sup>10</sup>

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<sup>8</sup> P. Putzeys and P. Van de Walle, *Bull. Soc. Chim. Biol.*, 1939, **21**, 185.

<sup>9</sup> L. S. Moyer and H. A. Abramson, *J. Biol. Chem.*, 1938, **123**, 391.

<sup>10</sup> R. A. Kekwick, *Biochem. J.*, 1938, **32**, 552.

## THE USE OF THIN LAYERS IN ELECTROPHORETIC SEPARATION.

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From the large-scale preparative point of view the usual U-tube principle in electrophoretic separation has several drawbacks. The percentage yield is limited by the fact that no boundary can be allowed to go round the bend in the U; the area available for passage of current is limited in one dimension by the required closeness of the cooling surface; the current density is limited by the ease with which convection is set up by horizontal temperature gradients; the facts that the voltage and heat produced are larger than they need be and that the heat is best removed at 4° C., have serious effects on the capital cost; and a substance whose mobility is intermediate between that of two others requires two successive runs for its isolation. Therefore, in spite of the high pitch of perfection to which Tiselius<sup>1</sup> has brought the U-tube apparatus, it seemed worth while to attempt to make an apparatus in which the U-tube principle is discarded altogether in favour of thin flowing layers. Considerable progress has been made in overcoming the many small difficulties involved; but at the moment of writing the apparatus must still be classed with those aeroplanes at South Kensington which never left the ground. The general position is that it will almost certainly, in favourable cases, separate substances far more rapidly than a U-tube apparatus of reasonable size; but that in the unfavourable cases, which are practically more important, difficulties become

<sup>1</sup> Tiselius, *Trans. Faraday Soc.*, 1937, **33**, 524.

apparent which set a definite though incalculable limit to the possibility of complete separation. The separation of anti-bodies, which is at present the most important possibility of electrophoresis, and which is easily done on a small scale by the Tiselius apparatus, lies very near to the limit for the thin-layer apparatus, and it is not yet possible to say on which side of the limit it lies. Even in extreme cases, however, the thin-layer apparatus can always in principle give results similar to those of the U-tube apparatus, namely, separation of a portion of the component having the greatest or least mobility. The U-tube principle was discarded by Theorell<sup>2</sup> in a semi-large-scale apparatus, but in such a way that only substances of opposite charge could be separated.

### Description of the Apparatus.

Fig. 1 shows diagrammatically the present form of the apparatus. It is made of "Perspex" and consists of entry slits A 1-5, exit slits B 1-6, anode C and cathode D. The exit slits are observed by a "schlieren"

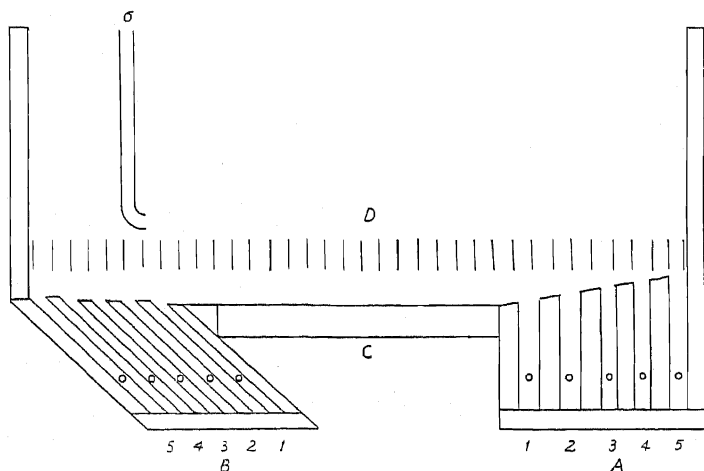


FIG. 1.

arrangement not shown, and the rates of flow are controlled by capillaries with reservoirs of adjustable height.

**The Entry Slits.**—The entry slits A 1-5 admit the following solutions, which are designed for the *pH* range covered by ammonia buffer.

1. 5 M. ammonium bromide, which acts as an anode liquid by liberating bromine, and also as a reserve of ammonium ion for the buffer.

2. 0.1 M. ammonium chloride, 0.005 M. ammonia, and 4 per cent. glycerol by volume. This is a buffer of the same composition as in the protein solution 3, made heavier by the glycerol.

3. 1.5 per cent. protein, 0.1 M. ammonium chloride, 0.005 M. ammonia, and 11 per cent. ethyl alcohol by volume. The *pH* is about 8.5 in this case.

4. The same as 3, without the protein. The alcohol and glycerol solutions, although having widely different densities, have the same refractive index, so that the schlieren arrangement only shows a faint line where they join, due to the difference in their diffusion constants. Thus it is easy to see the protein.

5. 0.5 M. ammonium chloride, 0.5 M. hydrochloric acid, and 40 per cent. by volume methyl alcohol. Probably the ammonium chloride

<sup>2</sup> Theorell, *Biochem. Z.*, 1935, 278, 291.

should be replaced by more hydrochloric acid. The latter was chosen for its high ratio of conductivity to density. The hydrogen ion cannot diffuse against the potential gradient, so the dilute buffer is unharmed by it. Methyl alcohol was chosen to lighten the solution in preference to ethyl, since its refractive index is lower so that its diffusion into the dilute buffer 4 causes less disturbance of the schlieren pattern.

The entry slits are fed with solutions through small holes at the bottom, and deliver them in fairly uniform layers without the trouble from air bubbles which rules out many other designs. They are, however, undergoing further improvement, as are the exit slits. Connection to the slits is made by the fine rubber tubing sold for bicycle tyre valves.

**The Anode.**—The anode C consists of a plate of gas carbon which has been impregnated with Perspex cement and then polished. The bromine produced stays in solution in the excess bromide, and being heavier is carried off in the bottom layer. The current density is about 0.3 amps./cm.<sup>2</sup>, and great difficulty was experienced in finding a continuous-flow anode which would carry this current without gassing. Even now there is some trouble from pockets of stationary solution where the carbon is cemented to the Perspex walls; but it seems that this can be avoided by careful construction.

**The Cathode.**—A continuous-flow non-gassing cathode does not seem to exist. Fortunately, however, it is possible so to design a gassing cathode that the underlying layers are undisturbed. It consists of a row of vertical strips of copper foil 5 or more mm. wide and 3 mm. apart, covering the whole area. It can be safely placed within a few millimetres of the dilute buffer 4.

**The Exit Slits.**—The five solutions flow quite smoothly on top of each other, over the very slightly inclined anode, till they are sorted out by the exit slits. By adjusting the rates of outflow any solution can be made to go down any slit, provided the order is maintained. The slit walls overhang so that two solutions entering the same slit mix as soon as they enter. This greatly decreases the time-lag of adjustment. Like the entry slits, the exit ones are wide and steep to avoid trouble from air bubbles. The thicknesses of the layers before leaving the cell are independent of the widths of the slits, but are controlled by the vertical distance between them. It is probably best to have slits Nos. 2-4 level, with 1 slightly lower and 5 slightly higher. Solution 1 is removed entirely by slit 1; solution 2 by slits 1 and 2; the wanted protein component in solution 3 by slit 3, and the unwanted components by slits 2 and 4; solution 4 by slits 4 and 5; and solution 5 by slit 5 and the suction tube 6. By determining the total rate of flow in slits 1 and 2 required to send any component into slit 3, with and without the electric migration, the mobility can in principle be obtained. The value will, of course, be affected by the glycerol and alcohol, but probably not enough to make the separation more difficult.

Apart from the theoretical difficulties discussed below the chief constructional difficulties are at present the prevention of gassing round the edges of the anode and the improvement of the slits so that they work well with all rates of flow and require less exact levelling. The present apparatus passes 6 amps. at 10 volts without stirring up the layers until the edges of the anode begin to gas; but as this happens fairly soon it is useless to attempt protein separations till the fault has been cured. However, a few encouraging tests have been made of the migration of hæmoglobin. The temperatures of the layers on leaving agree qualitatively with those predicted from the rates of flow, which are discussed below.

### Theoretical Considerations.

**1. Heat Production.**—It was pointed out by Tiselius<sup>1</sup> that the separation of a given volume of solution of given composition by electrophoresis requires the passage of a constant quantity of electricity independently of the shape of the apparatus. The heat evolved in the process does, however, depend on the shape of the apparatus and on the rate of separation. So far apparatus has been designed with a view to maximal rate of removal of heat rather than to minimal production of it. It is worth enquiring whether it is possible to make an apparatus in which the heat produced is so small that it need not be removed at all, but can be left in the solutions in the form of a harmless rise in temperature.

For simplicity consider a horizontal layer of protein solution of thickness  $p$  cm. which is sandwiched between layers of the solvent buffer solution, the whole in turn lying between suitable electrode solutions and plane electrodes as in the apparatus already described. Let the conductivity of the protein solution be  $K$ , assumed equal to that of its buffer, and let the two components to be separated differ in mobility by  $\delta\mu$ . If a vertical current  $i$  per cm.<sup>2</sup> is passed for time  $t$  the boundaries will separate by a distance

$$z_i = \frac{i t \delta\mu}{k} \quad (1)$$

When  $z_i = p$  the separation is complete, ignoring diffusion, and the time required for this is

$$t_p = \frac{k p}{i \delta\mu} \quad (2)$$

During this time the heat production has been

$$w = \frac{i^2}{k} \text{ watts per cm.}^3, \quad (3)$$

so that the rise in temperature, if no heat has been removed, is

$$\theta = 0.24 w t_p = \frac{0.24 i p}{\delta\mu} \quad (4)$$

Thus, theoretically, by diminishing  $i$  or  $p$  the rise in temperature accompanying the separation can be made as small as desired, in the absence of diffusion. Unfortunately the above conclusion no longer holds when diffusion is allowed for. Suppose that  $p$  is small compared with the final thickness of the diffusion layer, and let  $\sigma$  = the mass of dissolved protein per cm.<sup>2</sup>. Then the concentration at any point distant  $z$  from the middle of the layer after time  $t$  is given by

$$C = \frac{\sigma e^{-\frac{z^2}{4D_p t}}}{2(\pi D_p t)^{\frac{1}{2}}} \quad (5)$$

where  $D_p$  is the diffusion constant of the protein.<sup>3</sup> From (5) and the known values of the "probability integral" it follows that approximately 95 per cent. of the protein is included in a layer  $1.96 z_0$  thick, where

$$z_0 = \sqrt{8D_p t} \quad (6)$$

<sup>3</sup> Cf. W. Thomson, *Mathematical and Physical Papers*, Vol. II, p. 46, Section VIII, 1884.

To separate it, therefore, from a similar protein differing in mobility by  $\delta\mu$ , the current, from (1), must be

$$i = \frac{1.96k}{\delta\mu} \sqrt{\frac{8D_p}{t}}. \quad (7)$$

Hence, from (4), (6) and (7), the rise in temperature is

$$\theta_0 = 7.38 \frac{kD_p}{(\delta\mu)^2}. \quad (8)$$

The above expression for  $\theta_0$  is independent of current density or time. It is also practically independent of initial temperature, since the temperature coefficients of  $k$ ,  $D_p$ , and  $\mu$  are all nearly equal to that of the viscosity of water. If  $\theta_0$  is greater than the denaturation temperature then the proteins cannot be separated electrophoretically without removing heat by conduction either to neighbouring layers of solution or outside the apparatus. If  $\sigma$ , in equation (5), is replaced by the difference in concentration at a boundary between two thick layers one obtains the more familiar equation in which  $C$  is replaced by  $dC/dz$ . Thus the "separation temperature"  $\theta_0$  for preparative separation of thin layers is the same as that for optical separation of boundaries in the usual type of apparatus. In the latter case, however, preparative separation has only just begun when the optical separation is complete. Table I shows the separation temperature  $\theta_0$  in degrees Centigrade for

TABLE I.—SEPARATION TEMPERATURES. (For symbols see text.)

Substance.	Initial Temp. °C.	pH.	Salt.	$k \times 10^3$ .	$D_p \times 10^7$ .	$\delta\mu \times 10^5$ .	$\theta_0$ .
Phycocyan from Phycoerythrin <sup>1</sup>	0	6.96	0.01 M. phosphate acetate	0.77	2.2	10	0.13
Yeast flavo- protein from impurities <sup>4</sup>	20	4.65		1.19	6.28	3.8	3.8
Pepsin from impurities <sup>5</sup>	0	—	0.02 M. NaAc	0.8	5	ca. 2?	7.4
Horse anti- pneumococcus I from serum <sup>6</sup>	0	7.72	0.15 M. NaCl + 0.02 M. phosphate	9	2.2	0.9	181

four cases studied by other workers and illustrates how very much the ease of separation depends on the difference in mobilities and on the concentration of salt required to dissolve the protein.

All the equations so far given can be applied to the case where the layers are moving uniformly sideways with constant velocity  $s$ ; and the state at a distance  $x$  from the origin can be found by putting  $t = x/s$ . In the actual apparatus  $s$  is a function of  $z$ , so that the equations given are only approximations; but the equation

$$v = \frac{It\delta\mu}{k} \quad (9)$$

<sup>4</sup> Theorell, *Biochem. Z.*, 1935, 278, 270.

<sup>5</sup> Tiselius, Henschen and Svensson, *Biochem. J.*, 32, 1814.

<sup>6</sup> Tiselius and Kabat, *J. Exp. Med.*, 69, 119.

probably still holds exactly, where  $v$  is the volume traversed by the mid-point of the protein layer and  $I$  is the current. The total heat production is easily determined from the overall voltage. With the solutions described the present apparatus passes 6 amps. at 10 volts of which about 1 volt is chemical work. It therefore generates about 13 cal. per sec. The total flow of all solutions in the present experiments is about 0.5 ml. per sec., so the mean temperature rise, without external cooling, is about 26° C. This is not excessive and could easily be decreased by increasing the total flow; but in cases where  $\theta_0$  is high the problem is, as shown below, to combine a rapid total flow with a slow linear velocity of protein, and with rapid interchange of heat between the layers.

**2. Removal of Heat by Conduction.**—In the usual U-tube type of apparatus heat generated near the protein boundary is conducted away sideways. The horizontal density gradients so produced must be extremely small to avoid convection, and although Tiselius<sup>1</sup> made a great advance by working at the point of maximum density, the fact that temperature differences must be limited to about 0.5° C. is still a serious drawback. If heat could be removed by conduction downwards the temperature gradient would actually increase the stability, and the whole range from 0° C. to the denaturation temperature would be available as a driving force for conduction. Upward conduction of heat is also permissible provided that a favourable density gradient is produced by other means. There is another objection to horizontal cooling in a thin-layer continuous-flow apparatus, namely that the material in the immediate neighbourhood of a wall moves more slowly than the rest, so that it is exposed to the electric current for a longer time; for this reason the layers must be quite wide, and horizontal cooling would be very inefficient. Of the various possible methods of vertical cooling three will be considered: (a) a cooled lower electrode, (b) conduction into concentrated electrolyte, and (c) conduction into rapidly moving dilute electrolyte.

(a) Cooling the lower electrode by a stream of water underneath has the advantage over methods *b* and *c* that the stream can be as rapid as desired without any effect on the flow of solutions or cost of materials. The disadvantage is that the heat has further to travel so that the rate of conduction for a given temperature difference will be less. The lower limit to the distance travelled is set by the thickness of dilute buffer needed to prevent the concentrated electrode solution from diffusing into the protein. This thickness cannot be calculated even approximately for practical conditions, but can in practice be reduced to a few millimetres.

(b) The concentrated electrolyte forming the electrode solution will generate very little heat on passage of current, so will remove heat from the dilute layers above it. As it diffuses into the dilute electrolyte the latter will also generate less heat, and can take a corresponding amount from the protein layer. Unfortunately the cost of the ammonium bromide is an appreciable fraction of the running costs, so the flow of electrode solution should not be increased unduly.

(c) If some of the dilute electrolyte is made to move more rapidly than the protein layer it will carry away heat from the latter despite its equal electrical resistance. The relative velocities of different layers at the exits can be adjusted at will according to the heights of the slits and the rates of outflow; but this causes the layers to become

wedge-shaped, with the thin end pointing in the direction of relative motion. The angle of the wedge is decreased by increasing the difference in density or decreasing the difference in velocity. Within any wedge, ignoring diffusion, the velocity is a parabolic function of the height, and the constants of the parabola are fairly easily calculable. Thus it is possible to make both the upper and lower layers of dilute electrolyte move faster than the intermediate protein; but the difference in velocity will be less the further one goes from the exit. The wedge shapes so produced can be usefully applied to counteract the changes in thickness of the dilute buffer layer caused by diffusion of concentrated electrolyte.

The general conclusion from the above considerations is that if  $\theta_0$  is less than the denaturation temperature the proteins can be readily separated at current densities limited only by the electrodes; but that in cases where  $\theta_0$  is too high, so that conduction of heat between layers is required, the separability can only be determined by experiment. It will probably be found that there is a further upper limit to  $\theta_0$ , also independent of current density, below which complete separation is possible with vertical cooling and above which horizontal cooling, using very low current densities and thick layers, becomes preferable. It is possible that at high  $pH$ , and in presence of various non-electrolytes, sera can be kept in solution by lower concentrations of electrolyte than have been used. This may bring  $\theta_0$  for anti-bodies below the denaturation temperature, and greatly increase the ease of separation.

**3. Hydrostatic Stability of Floating Layers.**—Any layer will take up its proper position if its density is intermediate between that of its neighbours; but the diffusion boundary between two layers will become unstable if at any point the density gradient is positive upwards. For a boundary between two thick layers the maximum density gradient after time  $t$  is given by

$$\left(\frac{d\rho}{dz}\right)_{\max.} = \frac{1}{2\sqrt{\pi t}} \int \frac{(C_1 + C_2)}{\left(V - \frac{1}{\rho}\right)D \times 100} \quad (10)$$

Where  $\int$  denotes summation over all components,  $V$  is the partial specific volume of each,  $D$  the diffusion constant,  $C_1$  and  $C_2$  the concentrations in grams per cent. in the upper and lower layers respectively, and  $\rho$  the density of the solvent. Thus, if the summation term is negative the diffusion layer will be stable at all times. This applies *a fortiori* to thin layers, except in certain special cases. Using equation (10) it was calculated that the greatest permissible protein concentration in solution 3 above was 1.8 per cent. It could be increased by increasing the concentrations of glycerol and alcohol, which would be unwise in view of the fact that high concentrations of alcohol denature most proteins. The concentration of glycerol alone could be increased at the cost of some optical trouble. Ågren and Hammarsten<sup>7</sup> found that trypsin was uncharged in 30 per cent. glycerol at a  $pH$  where it was charged in water; this presumably means a shift in dissociation constants which might be compensated by changing the  $pH$ . For the present, however, it is best to consider the thin-layer apparatus as confined to fairly low protein concentrations, so that the current required per gram of protein separated is higher than it might be. The fact that

<sup>7</sup> Ågren and Hammarsten, *J. Physiol.*, 1937, 90, 330.

high concentrations involve boundary anomalies is some slight consolation for this.

**4. The Dilution Factor.**—The protein is diluted by diffusion during its passage through the apparatus, quite apart from the effect of any boundary anomalies. The dilution depends on the initial thickness of the protein layer and on the current density. The "separation temperature,"  $\theta_0$  above, was calculated on the assumption of a negligible initial thickness, which implies a large dilution. For any smaller dilution a factor  $f$  can be calculated by which  $\theta_0$  must be multiplied to obtain the modified separation temperature. If  $C_0$  is the initial concentration of the desired component and  $C_1$  its final average concentration in a sample containing 95 per cent. of the total amount, then the relation between  $f$  and  $C_1/C_0$  is given approximately by

$$\frac{C_1}{C_0} = 0.95 \cdot \left(\frac{3}{2}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}} (2f)^{\frac{1}{2}} e^{\frac{1}{2}} \left[ \int_{-\sqrt{2f}}^{+\sqrt{2f}} e^{-z^2} dz - 0.95 \right]. \quad (10)$$

provided  $C_1/C_0$  does not exceed about 0.5.

Table II gives values of  $C_1/C_0$  for various values of  $f$ . It shows that in order to limit the dilution to threefold or twofold the separation temperature must be increased by about 17 per cent. or 42 per cent. respectively.

**5. Running Costs.**—The chief drawback of the dilution is that it increases the quantity of electricity, and hence of electrode materials and buffer, needed to separate a given quantity of substance. The  $v$  of equation (9)

refers to the outflowing solution of concentration  $C_1$ . Hence if  $C_1$  is in grams per cent. and  $L$  is the cost per ampère-hour for current and materials then the cost per gram,  $l$ , is given by

$$l = \frac{Lk}{36C_1\delta\mu}. \quad (11)$$

The cost of current for the thin-layer apparatus is negligible, though for any apparatus using 500 volts or more it is the main item. The cost of electrode materials depends on the choice of electrode, which is largely determined by the current to be carried. A silver-silver chloride electrode has the advantage of being capable of regeneration, so that it uses only ammonium or sodium chloride; but it is very bulky, its capital cost is high, and it is not suited to continuous flow. Of the continuous-flow anode materials ammonium bromide makes a good compromise between cost and convenience costing  $\frac{1}{2}$ d. per ampère-hour for half-utilisation. The only material requirements peculiar to the thin-layer apparatus are methyl and ethyl alcohol and glycerol, which together cost 0.36 pence per ampère-hour in the case of the solutions described above. Although these running costs seem quite modest they are important in difficult separations, particularly because of the limit set to protein concentration in the thin-layer apparatus. For instance, at one penny per ampère-hour the purification of a 1.5 per cent. solution of 10 per cent. pure anti-body, with  $\delta\mu = 0.9 \times 10^{-5}$  and  $k = 0.0108$ , using a twofold dilution factor and

TABLE II.—DILUTION AND TEMPERATURE FACTORS.

$C_1/C_0$	$f$
0.12	1.02
0.33	1.17
0.39	1.25
0.45	1.33
0.49	1.42



ignoring boundary anomalies, costs about 37 shillings per gram. It would certainly be cheaper in a Tiselius U-tube apparatus. Thus the question of cost may well be the determining factor in deciding whether a given separation is better done in one or the other type of apparatus or whether it should be done by electrophoresis at all.

### General Conclusion.

It seems fairly clear that the apparatus here described should be readily applicable to several problems of purification; but the most important of all, the purification of anti-bodies, may prove to be just beyond its reach from the point of view of both heat production and cost of materials. It will probably depend on whether the conductivity of the buffer can be sufficiently diminished by various devices. There is little doubt that a thin-layer apparatus can give more rapid separation than any practicable U-tube apparatus; it may even prove capable of currents of 100 amps., since it can be enlarged in two dimensions. On the other hand any continuous flow apparatus will almost certainly need continuous attention, whereas one on the batch principle can be left unattended for long periods. This partly offsets the gain in speed.

*(Added in Proof.)* Since the above paper went to press the following further developments have occurred:—

(1) The flat anode has been replaced by five carbon rods 5 mm. in diameter, 1 mm. apart, and 2 mm. below the level of the lowest entry slit. The anode product is removed below the rods. With 5m ammonium bromide this arrangement can carry 6 amps. without gassing.

(2) Calculations have shown that the channels leading to the entry and exit slits should be as long as they are broad, and that the tubes should enter the channels at the bottom of the mid-line. A cell built on these lines gives very uniform flow.

(3) The present design of cathode causes less current to pass at the ends than in the middle. This causes convection sufficient to disturb the lower layers when 6 amps. are passing. The trouble should be easy to eliminate by proper design.

(4) The chief remaining difficulty is that the rise of temperature causes the formation of small air-bubbles which cling to the exit slits and disturb the flow. It may be necessary to degas all solutions before use or to work in the temperature range 0-15° C.

### Summary.

A large-scale electrophoretic separator is described in which the substance to be separated flows in a thin layer between layers of dilute electrolyte. The conditions for successful separation are discussed, and it is concluded that in favourable cases the apparatus has great advantages while in unfavourable ones there are difficulties which may interfere seriously with its practical application.

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# OBSERVATIONS AT THE ELECTROPHORETIC MOVING BOUNDARY WITH LAMM'S SCALE METHOD.

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The optical methods until recently used for the observation of the electrophoretic moving boundary, namely the light absorption and Toepler "schlieren" techniques, are not suited to the quantitative estimation of the amounts of components present in mixtures of proteins. The possibility of carrying out electrophoretic analyses by precision optical methods is very desirable in the examination of biological fluids such as sera, exudates and extracts of tissues and glands, etc. The observation of the moving boundary by means of Lamm's <sup>1</sup> scale method, the Philpot <sup>2</sup> "diagonal schlieren" method, and a recent modification of the latter by Svennson <sup>3</sup> renders such analysis practicable, following the introduction of the new Tiselius electrophoresis apparatus.<sup>4</sup>

This paper will be restricted to an account of the type of data obtainable by the use of the Lamm scale method, though essentially the same information can be obtained by the other two quantitative methods mentioned. These methods each make use of the differences in refractive index between the buffer and protein buffer solutions.

## Method.

A double equal distance scale situated about 4 cm. from the centre of the fluid column is photographed through the U-tube, one scale through each limb. A reference photograph is taken immediately after the formation of the boundary, the latter being at the time hidden by the centre plate of the U-tube. At suitable time intervals, after the circuit has been closed, further exposures are taken, and the line positions compared. Subtraction of the reference scale from the deviated scale for corresponding lines in the photograph gives a series of deviations  $Z$ , proportional to the gradient of refractive index at the position of the deviated scale line in the cell. The values of  $Z$  are then plotted against the deviated positions  $X$  in the cell. The scale line deviation  $Z$  is given by the equation:

$$Z = G \, ab \, \frac{dn}{dx} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the area enclosed by the curve

$$A = \int Z \, dx = G \cdot ab \int_{n_0}^{n_1} dn = G \cdot ab(n_1 - n_0) \quad . \quad . \quad (2)$$

<sup>1</sup> Lamm, *Z. physik. Chem.*, A, 1928, 138, 313; 1929, 143, 177. *Nova Acta Reg. Soc. Sci. Upsal.*, 1937, iv, 10, 6.

<sup>2</sup> Philpot, *Nature*, 1938, 141, 283.

<sup>3</sup> Svennson, *Kolloid Z.*, 1939, 87, 181.

<sup>4</sup> Tiselius, *Tran. Faraday Soc.*, 1937, 33, 524.

Where

$G$  = photographic enlargement factor.

$a$  = thickness of fluid column.

$b$  = optical distance from the scale to the centre of the fluid column.

$n_1$  = refractive index of the solution under observation.

$n_0$  = refractive index of the buffer in which the material is dissolved.

### Some Experimental Results and Discussion.

The progress of electrophoresis of a solution of crystallised egg albumin (0.55 per cent. in a phosphate buffer  $pH$  7,  $\mu = 0.05$ ) is shown in Figs. 1 and

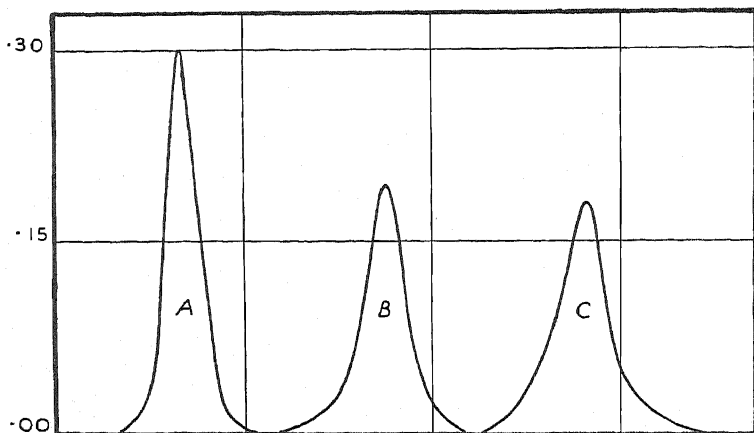


FIG. 1.—Anode limb curves.

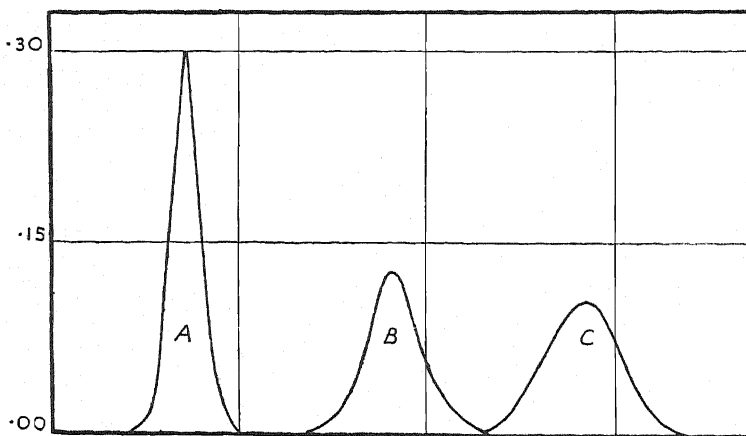


FIG. 2.—Cathode limb curves.

FIG. 1 and FIG. 2.—Electrophoresis of egg albumin. 0.55 per cent. egg albumin in phosphate  $pH$  7.0  $\mu = 0.05$ . Ordinate: scale line displacement in mm. Abscissa: distance in U tube in cm.

2, the curves being derived from corresponding exposures for the anode and cathode limbs respectively. Curve A shows the original boundary in each case before the circuit was closed, and curves B and C are from exposures taken 65 and 95 minutes after the potential was applied (5 volts/cm.). The position of the curves is arbitrary and bears no relation to the actual

migration; the abscissa scale, which represents cm. length in the U-tube, is included to give an idea of the spread of the boundaries.

It will be observed, that the shape of the curves differs in corresponding anode and cathode exposures, though the area can be shown to remain sensibly constant. It has been suggested by Longsworth and MacInnes,<sup>5</sup> that this effect is due to an increase in the potential gradient across the diffusion boundary from buffer to protein, occasioned by the higher viscosity of the protein solution. This would tend to cause a sharpening of the boundary migrating in the direction of the buffer, in this case on the anode side, and a broadening of the boundary migrating in the direction of the protein solution, in this case on the cathode side.

This modification of the process of normal diffusion at the boundary appears to be enhanced by increase of protein concentration and by the use of conditions causing a high mobility (e.g.  $pH$ 's much removed from the isoelectric point).

The type of behaviour to be expected in a mixture of proteins is exemplified by Fig. 3, a curve from the electrophoresis of a mixture of egg albumin and lactoglobulin (0.55 per cent. egg albumin, 0.51 per cent. lactoglobulin, in phosphate  $pH\ 8\ \mu = 0.1$ . Anode limb exposure after 4½ hours at 8 volts/cm.).

The mobilities of these two proteins are very close under the conditions used, and the separation achieved is not sufficient to warrant an analysis of the curve into the two simple curves corresponding to each component.

Figs. 4 and 5,<sup>6</sup> are electrophoretic diagrams of a normal human serum from the anode and cathode limbs respectively. (Phosphate  $pH\ 8\ \mu = 0.1$ , 5 volts/cm.,  $n_1 - n_0 = 0.00300$ .) Four protein components are evident,

TABLE I.

	Albumin.	Globulin.
Anode . .	58.8	41.2
Cathode . .	66.1	33.9

by each peak, which are proportional to the refractive increments due to each component. The extrapolations for the cathode curve are less certain, though the amounts of albumin and total globulin can be estimated with little error. The data shown in Table I. were obtained from the curves.

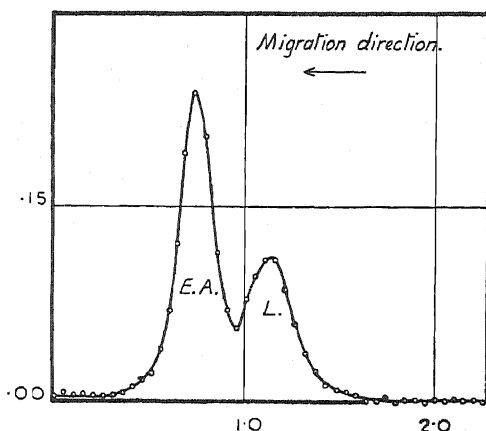


Fig. 3.—Electrophoresis of egg albumin—lactoglobulin mixture. 0.55 per cent. egg albumin, 0.51 per cent. lactoglobulin in phosphate  $pH\ 8.0\ \mu = 0.18$  volts/cm. Exposure 4½ hours after start. Anode limb. (E.A.) egg albumin. (L.) lactoglobulin. Ordinate: scale line displacement in mm. Abscissa: distance in U tube in cm.

albumin and  $\alpha$ ,  $\beta$  and  $\gamma$  globulins. A comparison of the curves for albumin in the two cases shows very markedly the effect discussed in connection with Figs. 1 and 2.

For the anode curve, slight extrapolations to the base line enable the estimation of the areas enclosed

<sup>5</sup> Longsworth and MacInnes, *Chem. Rev.*, 1939, 24, 271.

<sup>6</sup> Kekwick, *Biochem. J.*, 1939, 33, 1122.

The amounts of  $\alpha$ ,  $\beta$  and  $\gamma$  globulins found from the anode curve were 2.1, 10.0, 29.1 per cent. respectively.

The discrepancy between the anode and cathode values for albumin and globulin has been found consistently in many experiments, and in general the anode curves enclose slightly larger areas than the corresponding cathode curves. This is probably due to the inclusion in the anode curve of a " $\delta$  boundary"<sup>7</sup> with the  $\gamma$  globulin peak.

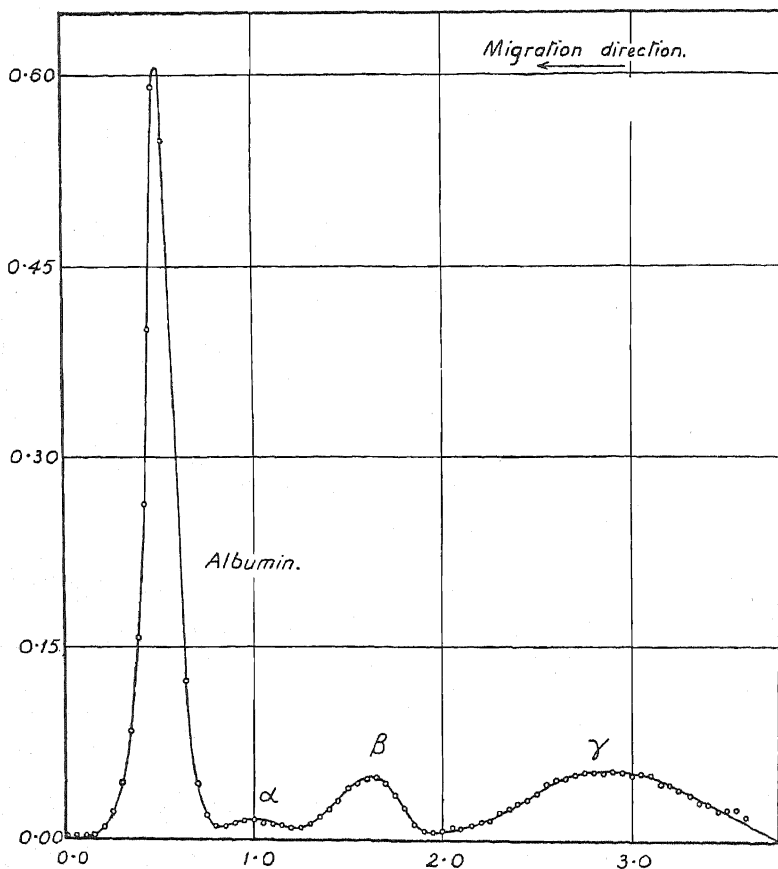


FIG. 4.—Electrophoresis of normal human serum. Anode limb phosphate, pH 8.0  $\mu = 0.1$   $n_1 - n_0 = 0.00300$ . 4.9 volts/cm. 152 min. after start. Ordinate: scale line displacement in mm. Abscissa: distance in U tube in cm.

The occurrence of a  $\delta$  boundary is limited to the anode limb and is more marked at high protein concentrations. It has been suggested by Longworth and MacInnes,<sup>5</sup> that the effect is due to differences in buffer salt concentration, between the buffer and protein solutions, caused by the establishment of a Donnan equilibrium during the initial dialysis against buffer. Svennson<sup>3</sup> in a recent paper has been able to correct for this effect but it was not possible to do so in the present case.

It has been shown<sup>6</sup> that the areas enclosed by curves such as those

<sup>7</sup> Tiselius, *Biochem. J.*, 1937, **31**, 1464.

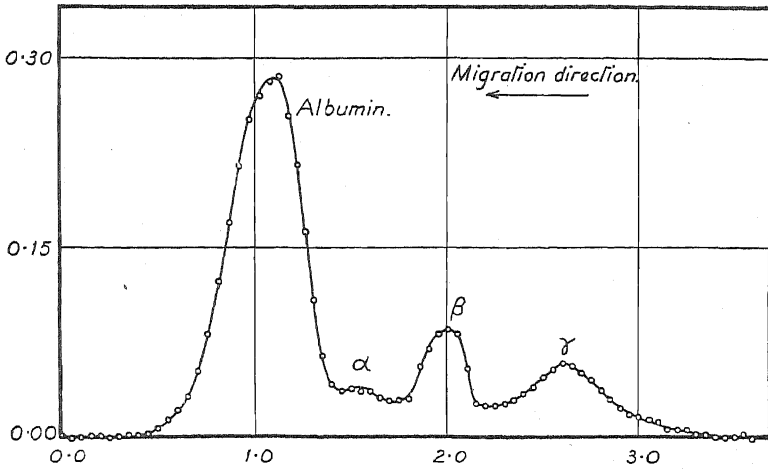


FIG. 5.—Electrophoresis of normal human serum. Cathode limb. Phosphate  $pH\ 8.0\ \mu = 0.1\ n_1 - n_2 = 0.00300$ . 4.9 volts/cm. 124 min. after start. Ordinate: scale line displacement in mm. Abscissa: distance in U tube in cm.

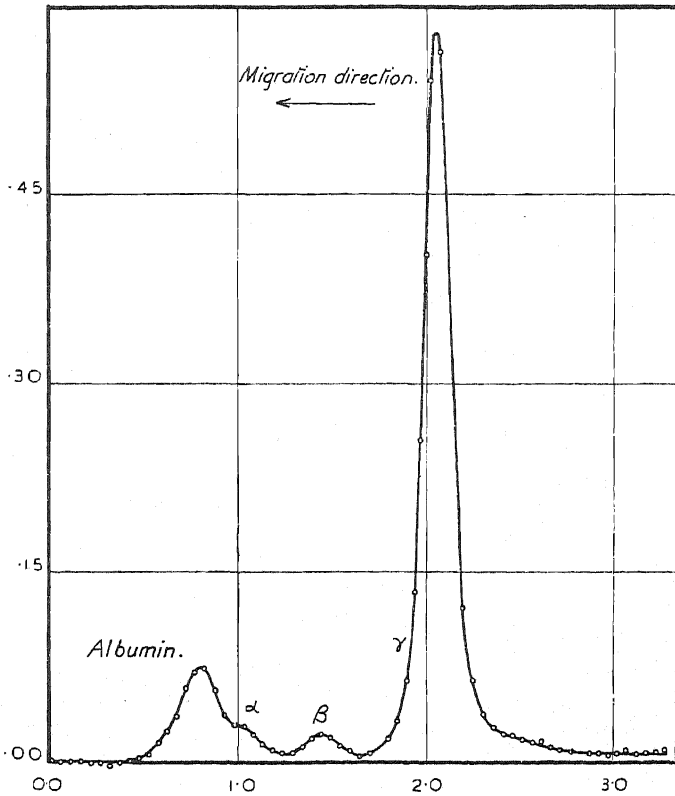


FIG. 6.—Electrophoresis of serum from a case of multiple myeloma. Anode limb. Phosphate  $pH\ 8\ \mu = 0.1\ n_1 - n_2 = 0.00270$ . 5 volts/cm. 90 min. after start. Ordinate: scale line displacement in mm. Abscissa: distance in U tube in cm.

under consideration is in reasonable agreement with the requirements of equation (2).

In certain pathological human conditions changes occur in the protein constitution of the sera which have been found consistent for a given disease. An extreme type of variation is shown in cases of multiple myeloma. This is illustrated in Fig. 6, an anode curve which should be compared with appearance of normal human serum as exemplified in Fig. 3. The analysis of Fig. 5 gives albumin 14.6 per cent.  $\alpha$ ,  $\beta$ , and  $\gamma$  globulin 2.2, 2.5 and 80.4 per cent. respectively.

The method has also been applied by Tiselius and Kabat<sup>8</sup> to the quantitative study of the changes occurring as a result of the absorption of specific antibodies from antisera.

### Summary.

A brief survey is given of the use of Lamm's scale method as a means of observation of the electrophoretic moving boundary.

Some examples of the type of data obtainable by this method are given and discussed.

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<sup>8</sup> Tiselius and Kabat, *J. Exp. Med.*, 1939, **69**, 119.

## AN EXAMINATION OF ELECTROKINETIC CHARGE DENSITY AS A FUNCTION OF THE THICKNESS OF THE DOUBLE LAYER.

By A. J. HAM AND E. D. M. DEAN.

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According to the well-known theory of Gouy,<sup>1</sup> the electrokinetic charge density ( $\sigma$ ) at an interface is related to the electrokinetic potential ( $\xi$ ) by ascribing to the effective thickness of the double layer a value  $1/\kappa$ , which is identical with the characteristic length term of the Debye-Hückel theory. D. C. Henry<sup>2</sup> has shown that a rather complex correction factor  $f(\kappa\alpha)$ , where  $\alpha$  is the radius of the particle, should be applied to the Smoluchowski equation which relates electrokinetic potential ( $\xi$ ) to electrophoretic mobility ( $u$ ):—

$$\xi = \frac{4\pi\eta u}{K} \frac{1}{f(\kappa\alpha)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where  $\eta$  and  $K$  are respectively the coefficient of viscosity and the dielectric constant of the medium. Combining this equation with

<sup>1</sup> Gouy, *J. Physique*, 1910, **9**, 457.

<sup>2</sup> D. C. Henry, *Proc. Roy. Soc., A*, 1931, **133**, 106.

those derived from Gouy's theory of the double layer, Henry has obtained :

$$u = \frac{\sigma\alpha}{\eta(1 + \kappa\alpha)} \cdot f(\kappa\alpha) \quad . \quad . \quad . \quad . \quad (2)$$

With the aid of these equations values of  $\zeta$  and  $\sigma$  may be calculated from mobility data.

It is found that as electrolyte is added  $\zeta$  falls regularly, after a very small initial rise observable in the presence of uni-univalent salts, but  $\sigma$  in general increases quite rapidly.<sup>3</sup> It will be noted that equation (1), which indicates a continuous fall in  $\zeta$  with decreasing mobility, involves no factor depending on the thickness of the double layer. The mathematical explanation of this rapid increase in the calculated charge density is clearly that  $1/\kappa$ , the thickness of the diffuse double layer, decreases so rapidly with added electrolyte, that even while  $\zeta$  falls,  $\sigma$  rises. Lewis and co-workers<sup>3</sup> have indicated that the physical meaning of this phenomenon is far from clear. In some cases where zero mobility is reached, both  $\zeta$  and  $\sigma$  must eventually reach zero; this would imply that  $\sigma$ , which appears to increase rapidly as electrolyte is added, falls to zero with a small further increase in electrolyte concentration. Moreover, it has been shown<sup>3</sup> that, at constant  $pH$ , a limiting value of mobility and of  $\zeta$  is often obtained—the isoelectric point never being reached; the charge density, however, continues to increase even in this case. It should be noted that we are here considering a case in which it is highly improbable that primary adsorption of added ions occurs, since the salts employed tend to raise the interfacial tension at an oil-water interface.

Since a variation, *i.e.*, a decrease, in  $1/\kappa$  can so easily over-compensate a decrease in  $\zeta$  (equation 2), the present investigation was undertaken with the object of studying variations in  $\zeta$  and  $\sigma$  at a value of  $1/\kappa$  which was maintained constant within small limits. Equations (1) and (2) were used to calculate  $\zeta$  and  $\sigma$  from the mobilities observed,  $1/\kappa$  being calculated as usual from the Debye-Hückel expression.

### Experimental.

The measurements of electrophoretic mobility were carried out macroscopically by the moving boundary method described by Price and Lewis,<sup>4</sup> and used by other workers.<sup>3</sup> The  $pH$  was maintained by the addition of small quantities of dilute hydrochloric acid to the dispersions, and was measured by means of a glass electrode in an oil thermostat at 25° C. In order to maintain well-defined boundaries, 2 per cent. of sucrose was contained in the dispersions, while the dispersion mixture and supernatant liquid (always of the same ionic composition) were brought to 25° C., before each experiment, and this temperature maintained during measurements.

Octadecane was chosen to supply the inert surface on which to observe the effects of salt addition. The initial material contained slight unsaturated impurities; repeated recrystallisation removed these impurities. Treatment with concentrated sulphuric acid or hydrogenation also gave fractions with the same ultimate mobility on recrystallisation. Dispersions prepared by the steam-jet, mechanical homogeniser or alcoholic

<sup>3</sup> Breese and Lewis, *Trans. Faraday Soc.*, 1938, 34, 787. Roberts, *ibid.*, 1936, 32, 1705.

<sup>4</sup> Price and Lewis, *ibid.*, 1933, 29, 775.



condensation methods gave identical mobilities at constant ionic composition of the dispersions; the alcoholic condensation method was used in most of the experiments.

In order to realise the desired conditions, *i.e.*, appreciable changes in mobility but a double layer of comparatively constant thickness, sufficient sodium chloride was added to reduce the thickness to a small value prior to the reduction in the mobility produced by additions of salts with higher valence cations. Further, octadecane particles are negatively charged, and hence mobility rises with increasing  $pH$ ; hence as high as a  $pH$  as practicable should be used in order to afford large and readily measured values of mobility. At  $pH = 5.5$  and above, great difficulty is encountered in maintaining a constant  $pH$  in unbuffered solutions; hence  $pH = 5.0$  has been used throughout.

### Discussion of Results.

#### Addition of Individual Salts.

The regular decrease in mobility on adding sodium, barium and lanthanum chlorides individually to octadecane dispersions, is shown in Table I; the values recorded are smooth values obtained by graphing the results.

The mobility does not fall to zero, but decreases logarithmically tending to limiting values dependent on the valency of the cation of the added salt, these values being approximately 4.0 for  $Na^+$ , 1.3 for  $Ba^{++}$  and 0.6 or less for  $La^{+++}$ . In the case of tristearin particles, Breese<sup>3</sup> found still higher values for these limiting mobilities. Such results suggest strongly that there is a limit beyond which salt addition can have no further electrokinetic effect. Table I indicates that, at any rate for  $Na^+$  and  $Ba^{++}$  where the limiting mobilities are relatively high in value, the charge density ( $\sigma$ ) steadily increases: the electrokinetic potential ( $\zeta$ ), however, falls regularly, and tends to a constant value. The limiting value of  $u$  in the case of lanthanum chloride is less than one unit.\* If the lanthanum ion were a little more effective, so that the limiting value were zero, then  $\sigma$  would necessarily reach zero also. The continued rise in  $\sigma$  is thus difficult to understand. Table I shows that it occurs as a result of the rapid fall in  $1/\kappa$  with increase in salt concentration: in very dilute lanthanum chloride solutions, the mobility is reduced rapidly enough to cause a decrease in charge density up to 0.00001 M. lanthanum chloride, at higher concentrations  $\sigma$  rises rather irregularly.

#### Addition of Salts in the Presence of 0.01 M. Sodium Chloride.

On the basis of Gouy's theory it follows that at a concentration of 0.01 M.  $NaCl$ ,  $1/\kappa$  is  $3.06 \times 10^{-7}$  cm. From Table I it is seen that in this case  $u$  is 6.7 units, at  $pH = 5.0$ . The further reductions in  $u$  occasioned by the addition of small amounts of barium or lanthanum chloride are recorded in Table II, together with the values of  $1/\kappa$ .

It is immediately clear that when  $1/\kappa$  is kept approximately constant, the charge density  $\sigma$  as well as the potential  $\zeta$  falls on the addition of salts with higher valency cations, which can reduce the mobility appreciably even in low concentrations. As soon as  $1/\kappa$  varies to an extent of some 10 per cent. in the case of barium chloride (0.001 M.),

\* The unit used is defined in Table I.

$\sigma$  follows its usual upward course. The range of concentration over which  $\sigma$  falls, on adding lanthanum chloride, is greatly enlarged by this fixation of the double layer by the device of adding 0.01 M. sodium

TABLE I.—MOBILITY OF OCTADECANE AT  $pH = 5$  AND AT  $25^\circ C$ .

Molar Concentration of Salt.	Mobility ( $\mu$ )* (Towards Anode.)	( $1/\kappa$ .)	Henry's Function, $f(\kappa\alpha)$ .	Charge Density, E.S.U. $\sigma$ .	$\zeta$ in Volts.
<i>Sodium chloride.</i>					
0	20.2	$9.71 \times 10^{-6}$	0.78	88	0.035
0.0001	15.5	2.92 "	.89	178	.023
0.0005	12.3	1.36 "	.94	282	.018
0.001	10.2	$9.62 \times 10^{-7}$	.95	323	.014
0.002	8.9	6.80 "	.97	389	.014
0.005	7.7	4.33 "	.98	521	.011
0.01	6.7	3.06 "	.98	641	.009
0.02	5.7	2.17 "	.99	761	.008
0.03	5.1	1.77 "	.99	833	.007
0.05	4.5	1.37 "	.99	949	.006
0.1	4.2	$9.71 \times 10^{-8}$	1.0	1235	.006
<i>Barium chloride.</i>					
0	20.2	$9.71 \times 10^{-6}$	0.78	88	0.035
0.000005	18.2	6.14 "	.82	113	.033
0.00005	10.8	2.42 "	.91	146	.018
0.000025	7.4	1.11 "	.95	203	.012
0.0005	6.0	$7.87 \times 10^{-7}$	.96	230	.009
0.001	5.0	5.59 "	.97	266	.008
0.0025	4.0	3.53 "	.98	331	.006
0.005	3.5	2.50 "	.98	409	.005
0.01	2.8	1.77 "	.99	458	.004
0.025	2.1	1.12 "	1.0	538	.003
0.05	1.5	$7.87 \times 10^{-8}$	1.0	542	.002
0.1	1.4	5.59 "	1.0	714	.002
<i>Lanthanum chloride.</i>					
0	20.2	$9.71 \times 10^{-6}$	0.78	88	.035
0.000001	15.7	7.63 "	.80	83	.026
0.000002	13.7	6.68 "	.81	82	.023
0.000005	10.6	4.83 "	.85	81	.017
0.00001	8.0	3.66 "	.88	75	.012
0.00002	6.7	2.68 "	.90	83	.010
0.00005	5.4	1.74 "	.93	98	.008
0.0001	4.4	1.24 "	.94	110	.006
0.0002	3.5	$8.80 \times 10^{-7}$	.96	123	.005
0.00025	3.2	7.87 "	.96	122	.005
0.0005	2.3	5.58 "	.97	122	.003
0.001	1.5	3.95 "	.98	116	.002
0.002	1.1	2.79 "	.99	114	.001
0.005	0.7	1.77 "	.99	115	.001
0.01	0.7	1.25 "	1.0	156	.001
0.02	0.6	$8.85 \times 10^{-8}$	1.0	194	.001

\* The unit of mobility employed is the velocity in cm. per sec. under 1 volt per cm., multiplied by  $10^6$ .

chloride. Up to a concentration of 0.005 M. lanthanum chloride,  $\sigma$  falls; but begins to rise again after that point.

Whether the Gouy theory leads to a correct estimate of the effective thickness of the diffuse layer or not, it may be safely assumed that, in

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the presence of a "swamping" concentration of sodium chloride this effective thickness is maintained constant, whatever its magnitude. Under this condition it is found that the values of  $\sigma$  (calculated on the Gouy theory) and the values of  $\zeta$  decrease together, which would be expected to happen on the now accepted structure of the double layer, *viz.*, that suggested by Stern. It would seem to follow that in those cases in which  $\sigma$  rises whilst  $\zeta$  falls, this abnormal and physically unacceptable behaviour of  $\sigma$  is not a physical reality but is merely a mathematical consequence of using Gouy's values of  $1/\kappa$ . The behaviour in fact is such as would arise from a value of  $1/\kappa$  which decreases far too

TABLE II.—MOBILITY OF OCTADECANE AT  $pH = 5$  AND AT  $25^\circ C.$ , IN THE PRESENCE OF  $0.01 M.$  NaCl.

Molar Concentration of Barium or Lanthanum Chloride.	Mobility ( $\mu$ ) Towards Anode.	$1/\kappa$ .	Henry's Function, $f(\kappa\alpha)$ .	Charge Density E.S.U. $\sigma$ .	$\zeta$ in Volts.
<i>Barium chloride.</i>					
0	6.7	$3.06 \times 10^{-7}$	0.98	641	0.009
0.00005	6.3	3.06 "	.98	602	.009
0.00025	5.9	3.05 "	.98	546	.008
0.0005	5.6	3.04 "	.98	538	.008
0.0025	5.1	2.95 "	.98	505	.007
0.005	4.9	2.85 "	.99	498	.006
0.0075	4.7	2.76 "	.99	492	.006
0.01	4.5	2.68 "	.99	480	.006
0.025	3.9	2.32 "	.99	487	.005
0.05	3.5	1.93 "	.99	523	.005
0.1	2.9	1.53 "	.99	548	.004
0.25	2.1	1.05 "	1.0	544	.003
0.5	1.5	$7.63 \times 10^{-8}$	1.0	681	.002
1	1.4	5.50 "	1.0	727	.002
<i>Lanthanum chloride.</i>					
0	6.7	$3.06 \times 10^{-7}$	0.98	641	0.009
0.00005	6.0	3.06 "	.98	574	.008
0.0001	5.5	3.05 "	.98	527	.008
0.0002	5.1	3.04 "	.98	491	.007
0.0005	4.5	3.01 "	.98	437	.006
0.001	3.8	2.97 "	.98	374	.005
0.002	3.2	2.89 "	.98	324	.004
0.005	2.3	2.68 "	.99	248	.003
0.01	1.9	2.42 "	.99	227	.003
0.02	1.5	2.06 "	.99	210	.002
0.05	0.8	1.53 "	.99	151	.001
0.1	0.7	1.16 "	1.0	173	.001
0.2	0.7	$8.49 \times 10^{-8}$	1.0	236	.001

rapidly with increasing concentration of electrolyte. It is probable, therefore, that some factor (not allowed for in the theory of Gouy) operates to allow of a much more moderate diminution in thickness of the layer on adding electrolyte. Of course, if this is true, none of the values of  $\sigma$  quoted can be regarded as absolute values; they are relative only.

## Summary.

(1) The electrophoretic mobilities of dispersions of octadecane in the presence of the chlorides of sodium, barium and lanthanum at  $25^\circ C.$  and a constant hydrogen ion concentration ( $pH = 5$ ) are recorded.

(2) The mobilities and potentials decrease regularly and tend to limiting values, depending on the particular cation added; while the charge density, as calculated on the basis of the theory of Gouy, rises throughout in the cases of sodium and barium chlorides and irregularly in the case of lanthanum chloride.

(3) This increase in charge density ( $\sigma$ ) depends on the rapid reduction in the thickness of the double layer,  $1/\kappa$ ; in very dilute solutions of lanthanum chloride the mobility and therefore  $\zeta$  is reduced with sufficient rapidity to give a decrease in  $\sigma$ .

(4) When the thickness of the layer is fixed by the addition of 0.01 M. sodium chloride, data are given to show that both electrophoretic charge density and potential fall as higher valency cations are added. Doubt is thus cast on the physical reality of the rising charge density values, with falling  $\zeta$  values, calculated on the basis of the Gouy theory. It is suggested that this theory demands far too rapid a decrease in thickness of the double layer with increase in electrolyte concentration.

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## THE PROPERTIES OF DETERGENT SOLUTIONS. PART IX.—THE ELECTROPHORETIC MO- BILITY OF OIL DROPS IN DETERGENT SOLUTIONS.

By J. POWNEY AND L. J. WOOD.

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Detergent action involves not merely the removal of dirt but also the stabilisation of the dirt in suspension in order to prevent its coagulation and redeposition on the surface being cleansed. In cases where there is a surface-active substance present in the solution, the interfacial energy of the dirt particles will be decreased by the formation of adsorbed films of the surface-active substance on their surfaces and consequently there will be less tendency for the particles to adhere to one another. Another factor which is probably of great importance is the magnitude of the zeta potential of the particles; those with high zeta potential will repel each other more strongly than those with a lower potential. Powis<sup>1</sup> has suggested that a minimum potential of 30 millivolts is necessary for the formation of a relatively stable oil-in-water emulsion, whilst Urbain and Jensen<sup>2</sup> have found that approximately the same potential is necessary for stable suspensions of carbon particles.

It is the purpose of the present paper to describe measurements of the electrophoretic mobility of highly refined mineral oil (Nujol) dispersed in water. The changes produced by the addition of various alkalies and surface-active substances in different concentrations have also been investigated.

Although there are numerous references in the literature<sup>3</sup> to the

<sup>1</sup> Powis, *Z. physik. Chem.*, 1914, **89**, 186.

<sup>2</sup> Urbain and Jensen, *J. Physic. Chem.*, 1936, **40**, 821.

<sup>3</sup> Cf. Valko, *Kolloidchemische Grundlagen der Textilveredlung*, Berlin, 1937; Clayton, *The Theory of Emulsions and their Technical Treatment*, London, 1935.

effect of electrolytes on the mobility of oil drops, there is very little information concerning the influence of surface-active substances. The most recent work appears to be that of Urbain and Jensen,<sup>2</sup> who have found that the mobility of oil drops and various other particles is greater in soap solutions than in water.

### Experimental.

An electrophoresis cell based on the same principle as that used by Smith and Lisse<sup>4</sup> was constructed. It consisted essentially of two cylindrical glass tubes, about 2 cm. in diameter, each containing a platinum electrode, the tubes being connected by two glass capillaries. The dimensions of the capillaries were carefully chosen so that the velocity of particles along the axis of the smaller capillary was the true electrophoretic velocity, the larger capillary acting as a return tube for the electro-osmotic flow of the dispersion medium. The velocity was determined by timing the passage of individual particles between two calibration lines in the eyepiece of a microscope, care being taken to avoid the possible error in focussing pointed out by Henry.<sup>5</sup> For each emulsion fifty readings were taken, the polarity of the electrodes being periodically reversed so that twenty-five were made in each direction.

The applied D.C. voltage was taken from a constant supply and could be varied by means of a potential divider over the range 0.250 volts. The actual voltage used depended on the order of the mobility to be measured, it having first been established that the mobility was independent of the applied voltage. The actual voltage was measured on a high resistance Ferranti moving coil voltmeter. For the most conducting solution, the current did not exceed 0.5 milliamp. and generally it was very much less than this. It was calculated that under these conditions the heating effect inside the capillaries was negligible. A thermometer was fixed in the cell for direct temperature reading. The experiments described below were all carried out at room temperature and the mobilities corrected to 25° C. on the assumption that for a given emulsion the mobility was inversely proportional to the viscosity of the dispersion medium which was, within experimental error, equal to that of water. Several times during each experiment the readings were interrupted and suction applied to one side of the cell in order to flush the capillaries. In this way the mobility measurements were not confined to any one small portion of the emulsion.

A stock emulsion of Nujol in water was prepared in the following manner. A solution of 1 gram of Nujol in 260 c.c. of boiling absolute alcohol was introduced through a fine jet into about one litre of hot distilled water. The emulsion thus obtained was boiled for about an hour to drive off the alcohol and water added to make up the volume to one litre. Emulsions prepared in this way remained stable for several weeks and were found to contain droplets of a convenient size ( $2-4\mu$ ). The diluted emulsions used in the cell were prepared by mixing equal volumes of the stock emulsion and solutions of the alkalis or detergents.

### Results and Discussion.

#### Mobility of Nujol in Water.

As a basis of comparison for the effect of alkalis and detergents on the electrophoretic mobility of Nujol it was necessary first to obtain an average value for the mobility of Nujol in pure water. As this value is very sensitive to minute traces of electrolytes,<sup>6</sup> an abnormally large number of

<sup>4</sup> Smith and Lisse, *J. Physic. Chem.*, 1936, 40, 399.

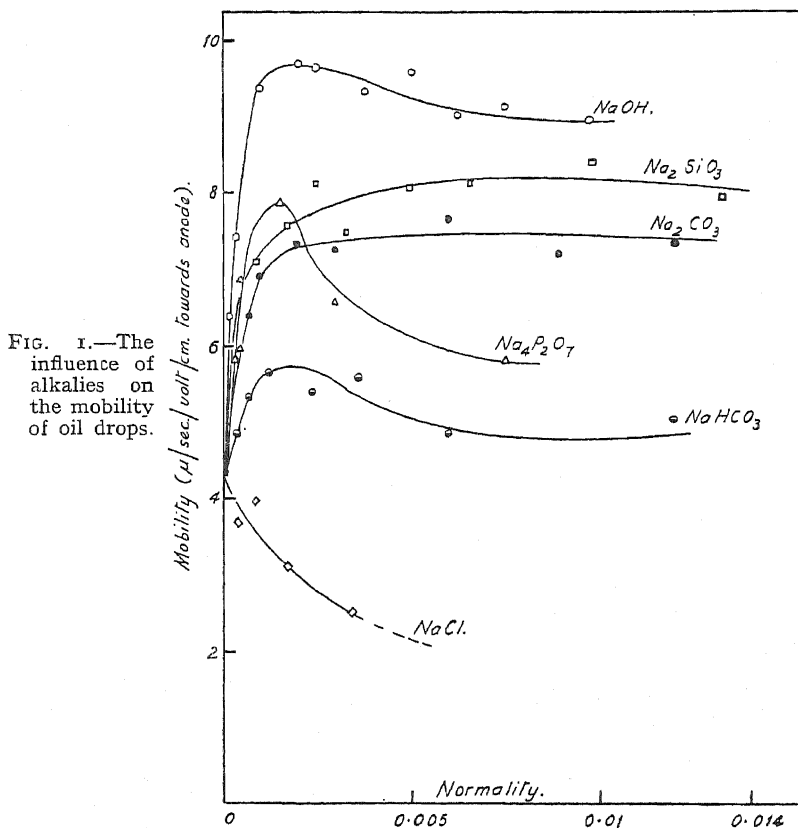
<sup>5</sup> Henry, *J.C.S.*, 1938, 997.

<sup>6</sup> Newton, *Phil. Mag.*, 1930 (vii), 9, 769.

determinations had to be carried out. The mean of 900 measurements made on six different Nujol dispersions in water of conductivity  $2 \times 10^{-6}$  ohm $^{-1}$  cm. was  $4.35 \mu/\text{sec.}/\text{volt}/\text{cm.}$  towards the anode at  $25^\circ \text{C.}$  The sensitivity of the water values to small quantities of impurities is reflected in the widely divergent values given in the literature for the mobility of paraffin oil in water. For example, Limburg<sup>7</sup> gives a value of  $3.65$  for  $25^\circ \text{C.}$ , whilst Urbain and Jensen's determination,<sup>2</sup> corrected to  $25^\circ \text{C.}$ , comes to  $6.65$ .

### Influence of Alkalies.

The mobility of suspended particles may be either decreased or increased by the addition of electrolytes, the direction and magnitude of



this change depending upon specific adsorption effects of the ions present.<sup>3</sup> In attempting to determine the influence of hydroxyl ion concentration on the mobility of Nujol, it was therefore necessary to investigate separately the influence of the sodium ion. Measurements on Nujol in sodium chloride solutions of various concentrations are shown in Fig. 1. Although it is not possible to neutralise the negative charge completely by addition of the sodium salt, a concentration of  $0.0035 \text{ N.}$  is sufficient to reduce the mobility to nearly one half of the water value. This value is in approximate agreement with, and intermediate between the observations of

<sup>7</sup> Limburg, *Rec. Trav. chim. Pays-Bas*, 1926, 45, 854.

Elis<sup>8</sup> and Tuorila.<sup>9</sup> At higher salt concentrations, the results tended to become very erratic. A very pronounced tendency for the Nujol to flocculate was noted under these conditions and this may account for the lack of reproducibility. It is interesting to note that the zeta potential at this critical point as calculated by Smoluchowski's equation is approximately 30 millivolts, the value which according to Powis<sup>1</sup> must be exceeded by a stable emulsion.

The effect of adding caustic soda, sodium metasilicate, sodium carbonate, sodium pyrophosphate and sodium bicarbonate is also shown in Fig. 1. With these alkalis a  $pH$  range of 8 to 12 is covered and there is now a progressive increase in the mobility with increasing  $pH$  value. In the presence of a fairly high hydroxyl concentration, therefore, the depressing action of the sodium ion is completely outweighed. A superimposed sodium ion effect may perhaps explain the tendency for the mobility to fall again at higher concentrations in the case of the alkalis of lower  $pH$  value.

### Influence of Surface-Active Substances.

The effect of long chain colloidal electrolytes on the electrophoretic mobility of oil drops will be determined partly by the formation of oriented

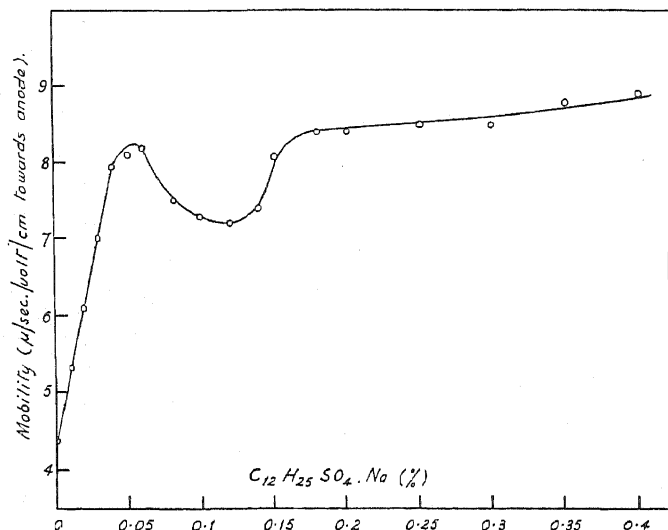


FIG. 2.—The mobility of oil drops in sodium dodecyl sulphate solutions.

interfacial films of the single long chain ions. It was thought that the well-known phenomenon of aggregation to form ionic micelles at certain critical concentrations<sup>10</sup> might be reflected in the electrophoretic behaviour of the oil drops.

Data for the influence of sodium dodecyl sulphate on the mobility of Nujol are plotted in Fig. 2. This substance is neutral in solution and therefore no  $pH$  effect arises. The curve obtained exhibits some interesting characteristics. The mobility first rises to a sharp maximum, which may be attributed to the adsorption of single long chain ions. The subsequent small but definite decrease of mobility is probably due to secondary adsorption of sodium ions. In the neighbourhood of the critical concentration of the dodecyl sulphate the mobility again rises sharply. A possible explanation of this behaviour is that in this region an increasing proportion of sodium ions becomes associated as gegenions with the ionic

<sup>8</sup> Ellis, *Z. physik. Chem., A*, 1912, **78**, 321.

<sup>9</sup> Tuorila, *Kolloid-Beih.*, 1926, **22**, 192.

micelles.<sup>10</sup> This would decrease the concentration of sodium ions free in the solution and consequently the superimposed sodium ion effect on the mobility of the oil drop would also become smaller.

The effect of dodecyl pyridinium chloride ( $C_{12}H_{25} \cdot C_5H_5N \cdot Cl$ ) on the mobility of Nujol has also been investigated over a wide range of concentrations (Fig. 3). It is noteworthy that only a very low concentration of the order of 0.0001 per cent. is necessary to reverse the sign of the net charge, due probably to the electrostatic attraction between the negative oil drops and the positive dodecyl pyridinium ions, whilst a concentration of only 0.01 per cent. is sufficient to give the maximum mobility. Under these conditions, it is possible that the long chain ions lie horizontally in the interface or even with their hydrocarbon chains oriented towards the aqueous phase. Glass vessels which have contained such solutions are rendered extremely and persistently hydrophobic. There is a slight falling off in the mobility at higher concentrations presumably due to a

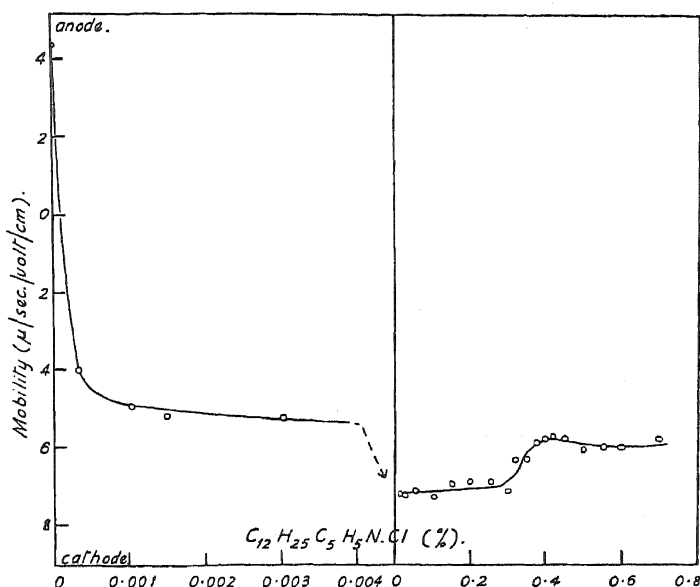


FIG. 3.—The mobility of oil drops in dodecyl pyridinium chloride solutions.

chlorine ion effect. This decrease in mobility is arrested, however, at a concentration of 0.4 per cent. Some recent surface tension measurements carried out in this laboratory indicate that the critical concentration for dodecyl pyridinium chloride is also approximately 0.4 per cent., so that the change in direction may arise from a gegenion effect similar to that discussed in connection with sodium dodecyl sulphate.

Measurements of the mobility of Nujol in sodium laurate and sodium oleate solutions have also been made in order to see whether hydrolysed long chain salts exhibit a similar behaviour. Curves are shown in Figs. 4 and 5 and it will be seen that the same critical changes occur as was found with sodium dodecyl sulphate. There is also shown in Fig. 5 the effect of suppressing the hydrolysis by the addition of 0.00975 N. caustic soda. As was anticipated the critical region is shifted towards lower concentrations, this no doubt being due to the fact that there is now no

<sup>10</sup> Hartley, *Aqueous Solutions of Paraffin-chain Salts*, Paris, 1936.



fraction of the soap present as insoluble acid soap aggregates. In each case the region of critical mobility occurs at a concentration agreeing with the critical concentration obtained from interfacial tension data.

FIG. 4.—The mobility of oil drops in sodium laurate solutions.

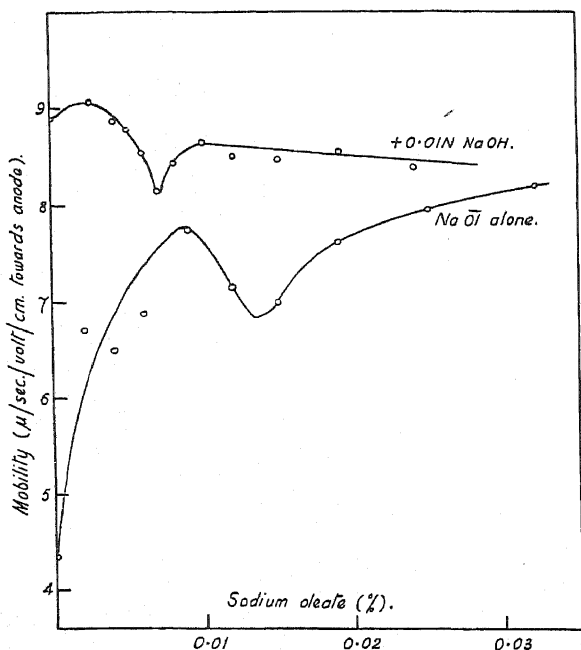
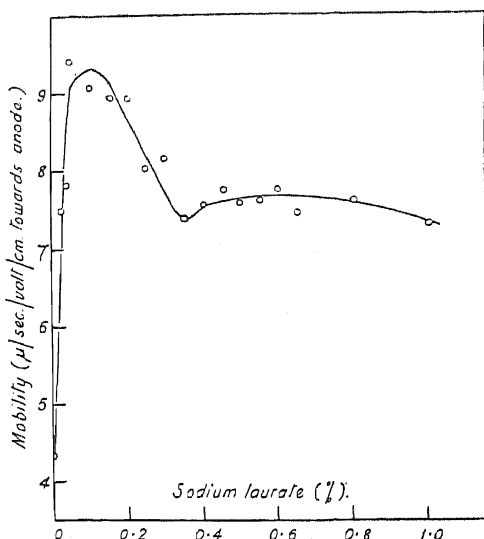


FIG. 5.—The mobility of oil drops in sodium oleate solutions.

### Summary.

Measurements of the electrophoretic mobility of highly refined mineral oil dispersed in water are described. A value of  $4.35\mu$ /sec./volt/cm. at  $25^\circ\text{C}$ . is obtained as the mean of nine hundred measurements.

Data concerning the influence of added alkalis on the electrophoretic mobility over a pH range of 8-12 are also recorded.

The electrophoretic mobilities of oil drops in the presence of sodium dodecyl sulphate, dodecyl pyridinium chloride, sodium laurate and sodium oleate have been determined over a range of concentrations and the results are discussed in relation to the constitution of colloidal electrolyte solutions.

The authors wish to thank the Director of Research for his valuable advice, and the Council of the British Launderers' Research Association for permission to publish this work.

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## ELECTROKINETICS XXIII. ELECTROKINETICS AS A TOOL FOR THE STUDY OF THE MOLECULAR STRUCTURE OF ORGANIC COM- POUNDS.\*

BY ROSS AIKEN GORTNER.

*Received 19th July, 1939.*

Electrokinetic studies have contributed much to our knowledge of colloidal behaviour and to conditions which exist at a solid-liquid interface. However, most of the studies have dealt with solid-aqueous solution interfaces and relatively few have been devoted to a study of solid-organic liquid interfaces. It seemed to the author that an exploration of this latter field might yield valuable information regarding the electrical behaviour of organic dipoles and accordingly, a series of studies has been initiated in which the behaviour of a group of *homologous series* of organic compounds has been investigated at various solid-liquid interfaces.

### Historical.

As early as 1861, Quincke<sup>1</sup> showed by electroösmosis that a number of solids which were negatively charged in contact with water became positively charged when in contact with turpentine. This was true of such diverse substances as silk, quartz, clay, asbestos, shellac, animal membranes, etc. Sulfur proved to be an exception, being negatively charged in both liquids. These observations were later extended by Coehn,<sup>2</sup> and Coehn and Raydt,<sup>3</sup> and resulted in the formulation of Coehn's rule that substances of a higher dielectric constant become positively charged when in contact with a liquid of a lower dielectric constant.

\* Paper No. 1724, Journal Series, Minn. Agric. Exp. Station.

<sup>1</sup> G. Quincke, *Pogg. Ann.*, 1861, 113, 513.

<sup>2</sup> A. Coehn, *Wied. Ann.*, 1898, 64, 217.

<sup>3</sup> A. Coehn and V. Raydt, *Drude's Ann.*, 1909, [4] 30, 777.

The next workers to study the electrokinetic behaviour of solid-organic liquid systems were Strickler and Mathews.<sup>4</sup> They studied the flow of organic liquids through a membrane of filter paper, again using electroendosmotic technique. They investigated the behaviour of a variety of organic liquids and found that while in a majority of cases the cellulose assumed a positive charge, nevertheless, this was not invariably true, since in contact with toluene, xylene, allyl alcohol, *iso*-amyl formate, *iso*-butyl formate and formamide the membrane was negatively charged. They state that Coehn's rule does not invariably hold and that an adsorption-orientation theory probably explains the origin and sign of the potential at the interface. The oriented layer of molecules produces a charge because of their polarity, and if dissociated molecules are present they effect the double layer by the specific adsorption of ions.

Fairbrother *et al.*<sup>5-7</sup> have likewise studied the electroendosmotic behaviour of organic liquids using carborundum, glass and sintered glass membranes. These authors calculated the *zeta*-potential at the interfaces, and related the potential to the dipole moment of the molecule by the formula

$$f = (D/M)^{\frac{1}{2}} \cdot \frac{\mu}{\eta} \quad (1)$$

where  $D$  = the density of the liquid,  $M$  = the molecular weight,  $\mu$  = the dipole moment of the molecule, and  $\eta$  = the viscosity.

When the electro-endosmotic velocity ( $V$ /c.c./sec./volt) was plotted against  $f$ , a straight line resulted for data from nitrobenzene, *o*-nitro-toluene, ether, *n*-propyl alcohol, *n*-butyl alcohol, benzaldehyde, aniline, and water. However, one exception was observed, for the acetone point fell far off of the straight line. These are the first studies relating the dipole moment of the molecule to electrokinetic behaviour, although such an effect is suggested by Strickler and Mathews.

Our studies, as already indicated, were undertaken to test the electrokinetic behaviour of *homologous series* of organic compounds with the view to (a) contribute to the theory of molecular structure, and (b) to possibly find an explanation for the specific biological reactivity of organic compounds, since a specific orientation of molecules on the various interfaces present within a biological organism must result from the adsorption of such molecules and a specific orientation should *a priori* alter the double layer at the interface, and accordingly change the electrical properties of the system. Since vital phenomena are so often manifested through electrical forces, it seemed reasonable to hope that electrokinetic studies might yield data of physiological value.

## Experimental.

**The Series Studied.**—We have completed studies,<sup>8-11</sup> of the aliphatic alcohols, the aliphatic acids, the ethyl esters of the aliphatic acids, the acetates of the aliphatic alcohols and a series of the derivatives of benzene.

<sup>4</sup> A. Strickler and J. H. Mathews, *J. Amer. Chem. Soc.*, 1922, **44**, 647.

<sup>5</sup> F. Fairbrother and M. Balkin, *J. Chem. Soc.*, 1931, 389.

<sup>6</sup> *Ibid.*, 1564.

<sup>7</sup> H. P. Dakin, F. Fairbrother and A. E. Stubbs, *ibid.*, 1935, 1229.

<sup>8</sup> W. McK. Martin and R. A. Gortner, *J. Physic. Chem.*, 1930, **34**, 1509.

<sup>9</sup> O. G. Jensen and R. A. Gortner, *ibid.*, 1932, **36**, 3138.

<sup>10</sup> M. Laufer and R. A. Gortner, *ibid.*, 1938, **42**, 641.

<sup>11</sup> *Ibid.*, 1939, **43**, 721.

Most of the compounds have been studied at both a cellulose-organic liquid and an  $\text{Al}_2\text{O}_3$ -organic liquid interface.

**The Electrokinetic Technique.**—Most of the other workers making studies of organic liquids have used electroendosmotic technique. We have found that the streaming potential technique, largely developed in our laboratories, is admirably adapted to studies of this type and in our hands it has proven to be simpler and to yield more readily reproducible data.

The apparatus which we have used is essentially that developed by Briggs,<sup>12</sup> although the streaming cell has been modified from time to time,<sup>8, 10</sup> as has the wiring diagram.<sup>12, 8</sup> A quadrant electrometer has, in all cases, been used as the null instrument. The latest and most easily utilizable form of the streaming cell is shown in Fig. 1. The solid to be studied is packed in the central portion of the cell and the organic liquid is then streamed through the diaphragm from one reservoir to the other under a known and controlled hydrostatic pressure.

In the earlier studies calculations of the  $\zeta$ -potential were made by the well-known formula

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon} \quad (2)$$

where  $\zeta$  = the zeta potential,  $\eta$  = the coefficient of viscosity,  $H$  = the observed E.M.F.,  $\kappa_s$  = the specific conductivity of the liquid in the diaphragm (including surface conductance),  $P$  = the hydrostatic pressure,  $\epsilon$  = the dielectric constant. In later work we have found the expression " $\delta e$ " to be preferable. This expression arises from the equation

$$\delta e = \frac{\eta\kappa_s H}{P} \quad (3)$$

where  $e$  = the charge per sq. cm. of the double layer and  $\delta$  = the thickness of the double layer.

The values for  $\delta e$  may be regarded as the electric moment of the double layer. Since it has been shown<sup>13</sup> that changes in the  $\zeta$ -potential involve both charge and distance separating charges in the double layer, and also since equation (3) involves no assumption as to the magnitude of the dielectric constant across the double layer, but involves only those quantities which can be easily measured, it seems to be the preferable equation to use.

**The Experimental Data.**—The experimental data are summarised in Table I.

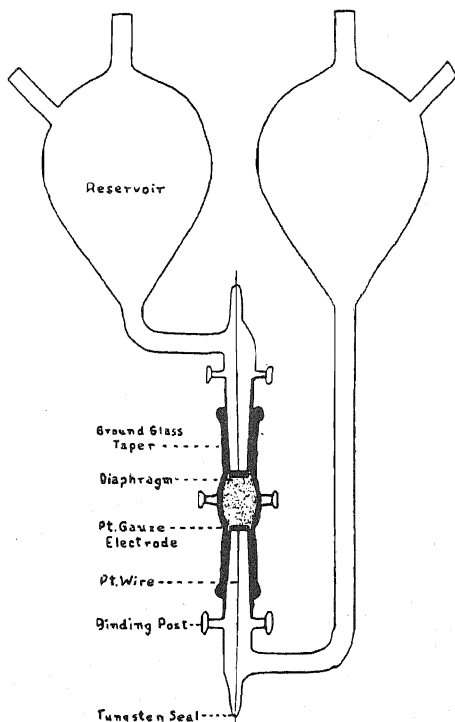


FIG. 1.—Streaming cell for electrokinetic studies.

<sup>12</sup> D. R. Briggs, *J. Physic. Chem.*, 1928, **32**, 641.

<sup>13</sup> H. B. Bull and R. A. Gortner, *J. Physic. Chem.*, 1931, **35**, 309.

TABLE I.— $\zeta$ -POTENTIAL AND ELECTRIC MOMENT ( $\delta e$ ) PER UNIT AREA OF THE DOUBLE LAYER AT INTERFACES BETWEEN CELLULOSE OR  $Al_2O_3$  AND CERTAIN PURE ORGANIC LIQUIDS.\*

Organic Liquid.	Cellulose-Liquid Interface.		$Al_2O_3$ -Liquid Interface.	
	$\zeta$ -potential (mv.).	$\delta e$ (e.s.u. $\times 10^6$ ).	$\zeta$ -potential (mv.)	$\delta e$ (e.s.u. $\times 10^6$ ).
Methyl alcohol . .	— 55.3	— 47.8	— 26.7	— 218.0
Ethyl alcohol . .	— 19.9	— 13.6	— 14.7	— 94.2
<i>n</i> -propyl alcohol . .	+ 17.1	+ 9.8	— 11.7	— 64.7
<i>iso</i> -propyl alcohol . .	— 16.2	— 11.4	+ 11.5	+ 73.6
<i>n</i> -butyl alcohol . .	+ 51.7	+ 27.0	— 3.7	— 17.8
<i>iso</i> -butyl alcohol . .	+ 12.4	+ 7.6	+ 2.0	+ 10.2
<i>n</i> -amyl alcohol . .	—	—	+ 8.9	+ 36.8
<i>n</i> -hexyl alcohol . .	+ 33.6	+ 11.9	+ 35.3	+ 122.4
<i>n</i> -heptyl alcohol . .	— 6.6	— 18.7	+ 8.9	+ 26.0
Acetic acid . .	+ 5.27	+ 8.74	+ 39.4	+ 65.2
<i>n</i> -propionic acid . .	+ 1.31	+ 1.12	+ 18.7	+ 16.7
<i>n</i> -butyric acid . .	— 0.48	— 0.35	+ 17.4	+ 13.0
<i>n</i> -valeric acid . .	— 1.11	— 0.77	+ 12.1	+ 8.4
<i>n</i> -caproic acid . .	— 1.67	— 1.40	+ 29.0	+ 24.8
Ethyl formate . .	— 6.31	— 11.80	+ 113.0	+ 212.0
Ethyl acetate . .	— 3.42	— 5.72	— 24.8	— 41.4
Ethyl <i>n</i> -propionate . .	— 2.06	— 3.02	— 10.8	— 29.0
Ethyl <i>n</i> -butyrate . .	— 2.09	— 2.85	— 32.1	— 43.6
Ethyl <i>n</i> -valerate . .	— 3.67	— 4.71	—	—
Ethyl <i>n</i> -caproate . .	— 4.52†	— 5.33	—	—
Ethyl <i>n</i> -heptylate . .	— 3.81†	— 4.14	—	—
Methyl formate . .	— 10.10	— 22.30	—	—
Methyl acetate . .	— 7.35	— 13.65	— 21.7	— 38.8
Ethyl acetate . .	— 3.42	— 5.72	— 24.8	— 41.4
<i>n</i> -propyl acetate . .	— 1.89	— 3.13	— 19.2	— 31.7
<i>n</i> -butyl acetate . .	— 2.70	— 3.67	— 20.6	— 27.5
<i>n</i> -amyl acetate . .	— 1.59	— 2.11	— 9.5	— 12.6
Benzene . .	0.00	0.00	—	—
Methylbenzene . .	— 0.2	— 0.13	—	—
Chlorbenzene . .	— 1.0	— 1.51	—	—
Brombenzene . .	— 6.7	— 9.71	—	—
Aminobenzene . .	— 49.7	— 99.56	—	—
Nitrobenzene . .	— 142.0	— 1390.0	—	—
Carbon tetrachloride . .	0.00	00.00	—	—

\* Note: The sign indicates the sign of charge on the solid side of the interface. The streaming liquid would accordingly possess the opposite charge.

† Dielectric constant obtained by extrapolation.

### Discussions and Conclusions.

Perhaps the data on homologous series are still too inadequate to permit of generalised conclusions. It is evident, however, that the sign and magnitude of the electric double layer at solid-organic liquid interfaces is a function not only of the polarity of the organic liquid but also of the specific solid with which the liquid is in contact. It is obvious from the data that Coehn's rule does not hold invariably and, in fact, appears to have no validity.

In all cases but one the electric moment of the double layer is much higher in  $\text{Al}_2\text{O}_3$ -organic liquid systems than it is in the corresponding cellulose-organic liquid system. This must be due either to a greater degree of orientation of the organic molecules at the  $\text{Al}_2\text{O}_3$  interface or to a greater dissociation of the organic molecules at the  $\text{Al}_2\text{O}_3$  interface.

The origin of these potentials presents an interesting problem. We are not accustomed to think of organic liquids as dissociating appreciably into ions, nevertheless, the high potentials which can be produced by the streaming potential technique, *e.g.* 109.8 v. for an *n*-propyl acetate-cellulose system under 5.57 cm. Hg pressure, or 88.59 v. for an  $\text{Al}_2\text{O}_3$ -*n*-caproic acid system under 5.82 cm. Hg pressure, can only be accounted for by assuming a transfer of ions from one electrode to the other. Possibly the charge density at the interface is produced by a specific adsorption of either anions or cations, but it is difficult to explain why the alcohol-ionium ion should be adsorbed by cellulose from *n*-propyl alcohol and the alcoholate ion from *iso*-propyl alcohol, and why the adsorption of the reverse ions should be characteristic of  $\text{Al}_2\text{O}_3$ . The same reversal of sign between *n*-butyl and *iso*-butyl alcohols occurs in an  $\text{Al}_2\text{O}_3$ -alcohol system, but in a cellulose-alcohol system these two alcohols yield the same sign of charge. Similarly, in the case of the aliphatic acids, the  $\text{Al}_2\text{O}_3$ -acid systems all yield the same charge sign, whereas in the cellulose-acid systems the charge is reversed between propionic and butyric acids. All esters in both systems yield a negative interface except for ethyl formate- $\text{Al}_2\text{O}_3$ , where the charge is positive and very high. Apparently, the pseudo-aldehyde group of the formate molecule is exerting a preponderant effect. An amazing regularity of a difference of approximately 35 mv. in the magnitude of the  $\zeta$ -potential between the members of the homologous series of the *normal* aliphatic alcohols in the alcohol-cellulose series is one of the striking findings of this series of studies, as is the close similarity of the behaviour of the *iso*-alcohols to that of the *n*-alcohol of the next lower member of the series, thus, *iso*-propyl alcohol more nearly resembles ethyl alcohol and *iso*-butyl alcohol more nearly simulates *n*-propyl alcohol.

In the benzene series, on which unfortunately we still have limited data, the striking effect of various mono-substituents in the molecule is noteworthy. The high electric moments of the interfaces at cellulose-aniline, and cellulose-nitrobenzene indicate either great specific ionic adsorption or a great distortion of the electric fields in adsorbed molecules. It may well be that a specific surface *forces* a dissociation of these organic molecules, and in this phenomena may lie the answer to catalytic phenomena. Invertase, for example, "dissociates" sucrose into its component parts, and it may well be that further electrokinetic studies such as these will contribute an explanation not only to catalytic behaviour but to various other physiological and technological processes.

If, in catalysis, a given solid interface does "force" a "dissociation" of organic molecules, and if then either the "anion" or "cation" is strongly adsorbed by the solid, we should expect an  $\text{Al}_2\text{O}_3$ -*n*-propyl alcohol system to yield somewhat different end products than those yielded by an  $\text{Al}_2\text{O}_3$ -*iso*-propyl alcohol system, since the double layers show reversed orientation. In view of the present data, this would appear to be a profitable field for investigation. Similarly, it would be interesting to know how the different forms of  $\text{Al}_2\text{O}_3$ , known to differ in adsorption behaviour and in catalytic activity, would behave electrokinetically against the same series of organic liquids.

The above are only a few of the problems that this series of studies has suggested. We propose to extend the studies as opportunity permits. The few studies which have been made do, however, indicate that a study of the electrokinetic behaviour of pure organic liquid solid interfaces can contribute important and valuable data to our knowledge of the molecular structure of organic compounds, and while the data as yet are not readily interpretable in terms of theory, they present somewhat of a challenge demanding further investigations.

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# PART I.—(B) STREAMING EFFECTS AND SURFACE CONDUCTION.

## STREAMING POTENTIALS AND SURFACE CONDUCTANCE.

BY A. J. RUTGERS.

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### 1.

The fundamental quantity in colloid chemistry is the electrokinetic potential  $\zeta$ ; the  $\zeta$ -potential determines, *e.g.*, the stability of colloidal solutions, the electrophoretic velocity of colloid particles, etc. Therefore it is of interest to have at disposal a method by means of which  $\zeta$ , and in the first place the dependence of  $\zeta$  on the concentration of electrolyte, can be studied. Such a method is provided by the streaming potentials.

The streaming potential  $E_1$ , the electrostatic potential difference which occurs between the ends of a capillary of radius  $r_1$ , when a liquid (dielectric constant  $D$ , specific electric conductivity  $\sigma$ , viscosity  $\eta$ ) is pressed by a hydrostatic pressure  $P$  through that capillary, is given by the Helmholtz-Smoluchowski equation:<sup>1</sup>

$$\frac{E_1}{P} = \frac{D\zeta(c)}{4\pi\eta\sigma(c)}. \quad . \quad . \quad . \quad . \quad (1)$$

Derivation: In the case of water, pressed through a glass capillary, the wall is negatively, the liquid positively, charged. These positive charges are carried with the liquid (convection of electric charge); if the length of the capillary is  $l$ , the radius of the circular section  $r_1$ , the velocity of the liquid in the capillary  $v(r)$  is given by:

$$v(r) = \frac{P}{4\eta l} (r_1^2 - r^2) \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{dv}{dr} = -\frac{Pr}{2\eta l} \quad . \quad . \quad . \quad . \quad (3)$$

The gradient of the velocity at the wall is

$$\left(\frac{dv}{dr}\right)_{r=r_1} = -\frac{Pr_1}{2\eta l} \quad . \quad . \quad . \quad . \quad (4)$$

The diffuse electric charge in the liquid is situated in the immediate neighbourhood of the wall; the thickness of the diffuse layer is very small in comparison with the radius of the capillary; therefore, in the

<sup>1</sup> M. v. Smoluchowski, *Graetz' Handbuch*, II, p. 374.



calculation of the transport of electric charge by convection, the wall of the capillary may be considered to be flat.

The velocity of the liquid in the immediate neighbourhood of the wall, at a distance  $x$  from the wall, will be

$$v(x) = \left( \frac{dv}{dx} \right)_{x=0} x = \frac{Pr_1}{2\eta l} x. \quad (5)$$

The electric charge carried away per second amounts to

$$I_1 = 2\pi r_1 \int_0^\infty \rho(x)v(x)dx = -2\pi r_1 \int_0^\infty \frac{D}{4\pi} \frac{Pr_1}{2\eta l} \frac{d^2\psi}{dx^2} x dx = \\ - \frac{DPr_1^2}{4\eta l} \left[ x \frac{d\psi}{dx} \right]_0^\infty + \frac{DPr_1^2}{4\eta l} \int_0^\infty \frac{d\psi}{dx} dx = -D\zeta r_1^2 \frac{P}{4\eta l}. \quad (6)$$

This transport of charge will cause an electric potential difference  $E_1$  between the ends of the capillary, which will give rise to a current of conduction  $I_2$  given by

$$I_2 = \sigma \frac{E_1}{l} \pi r_1^2. \quad (7)$$

In the stationary state  $I_1 + I_2 = 0$ , and therefore

$$\frac{E_1}{P} = \frac{D\zeta}{4\pi\eta\sigma} \quad (1)$$

which is the Helmholtz-Smoluchowski equation; the length  $l$  and the radius  $r_1$  of the capillary do not appear in the final equation.

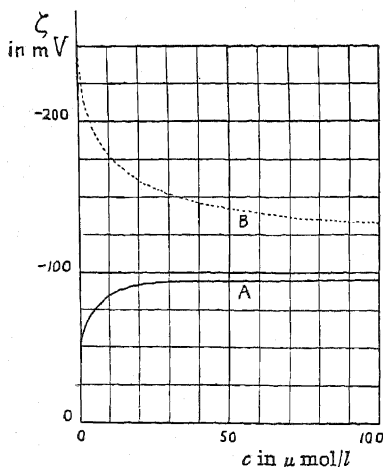


Fig. 1.— $(\zeta)_{\text{obs.}}$  (curve A) and  $(\zeta)_{\text{theor.}}$  (curve B) as a function of concentration.

Krulyt and his collaborators<sup>2</sup> and Freundlich and Ettisch<sup>3</sup> have carried out measurements of streaming potentials on aqueous solutions containing very small amounts of electrolyte (KCl,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{ThCl}_4$ , respectively, KCl,  $\text{BaCl}_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Th}(\text{NO}_3)_4$ ); in the most simple case, the one of KCl, a curve giving  $\zeta$  as a function of concentration is obtained of the form shown in Fig. 1 (curve A). The shape of this curve is rather unexpected; the theory leads one to a curve shaped like B.

This discrepancy between theory and experiment can be removed in the following way: various authors, e.g.,

Smoluchowski,<sup>4</sup> Briggs,<sup>5</sup> Bull and Gortner,<sup>6</sup> and especially in connection

<sup>2</sup> H. R. Krulyt, *Proc. Kon. Akad. v. Wetensch. Amsterdam*, 1914, **17**, 615, 1917, 19, 1021; H. R. Krulyt and P. C. van der Willigen, *Koll. Z.*, 1928, **45**, 307; P. C. van der Willigen, *Thesis*, Utrecht, 1927; L. W. Janssen, *Thesis*, Utrecht, 1937.

<sup>3</sup> H. Freundlich and G. Ettisch, *Z. physik. Chem.*, 1925, **116**, 401.

<sup>4</sup> M. v. Smoluchowski, *Physik. Z.*, 1905, **6**, 529.

<sup>5</sup> D. R. Briggs, *J. Physic. Chem.*, 1928, **32**, 641.

<sup>6</sup> H. B. Bull and R. A. Gortner, *J. Physic. Chem.*, 1931, **35**, 309.

with the problem considered here, Bikerman,<sup>7</sup> have drawn attention to the fact, that the quantity  $\sigma$  in (1) designates the specific electric conductivity of the liquid *in the capillary*; so that, if experiments are made with very dilute solutions (*i.e.* with very pure water), the surface conductance will come into play, especially when the capillary is very narrow. If  $\sigma_0$  is the specific electric conductivity of the liquid in bulk,  $\sigma_w$  the specific surface conductivity, (7) must be replaced by:

$$I_2 = \frac{E_1}{l} \left[ \sigma_0 \pi r_1^2 + \sigma_w 2\pi r_1 \right] = \frac{E_1}{l} \sigma_0 \pi r_1^2 \left( 1 + \frac{2\sigma_w}{r_1 \sigma_0} \right) \quad (8)$$

and instead of (1) we obtain:

$$\frac{E_1}{P} = \frac{D\zeta}{4\pi\eta\sigma_0} \frac{1}{1 + \frac{2\sigma_w}{r_1\sigma_0}} \quad (9)$$

or 
$$\zeta = \frac{4\pi\eta}{D} \sigma_0 \frac{E_1}{P} \left( 1 + \frac{2\sigma_w}{r_1\sigma_0} \right) = \zeta_1 \left( 1 + \frac{2\sigma_w}{r_1\sigma_0} \right) \quad (10)$$

where 
$$\zeta_1 = \frac{4\pi\eta}{D} \sigma_0 \frac{E_1}{P} \quad (11)$$

In other words, the true value of  $\zeta$  is obtained by multiplying the apparent value  $\zeta_1$  by a factor greater than unity, and it is greater as the value of  $\sigma_0$  is smaller, *i.e.*, as the water is purer. Returning to Fig. 1 we see that, if the values of  $(\zeta)_{\text{obs.}}$ , which we now call  $\zeta_1$ , are multiplied by a factor greater than unity for small concentrations, and approaching unity for larger concentrations, we may obtain a curve of the shape of  $(\zeta)_{\text{theor.}}$ .

On the other hand, if we write

$$\zeta_1 = \frac{\zeta}{1 + \frac{2\sigma_w}{r_1\sigma_0}} \quad (12)$$

we see that the apparent value of the electrokinetic potential  $\zeta_1$ , calculated from experimental data by means of (11), will depend on the radius of the capillary employed, and will be the smaller the narrower the capillary.

Therefore, if measurements are made with three capillaries of exactly the same material, and of increasing radii  $r_1, r_2, r_3$ , we must expect curves for  $\zeta_1, \zeta_2, \zeta_3$  as shown in Fig. 2.

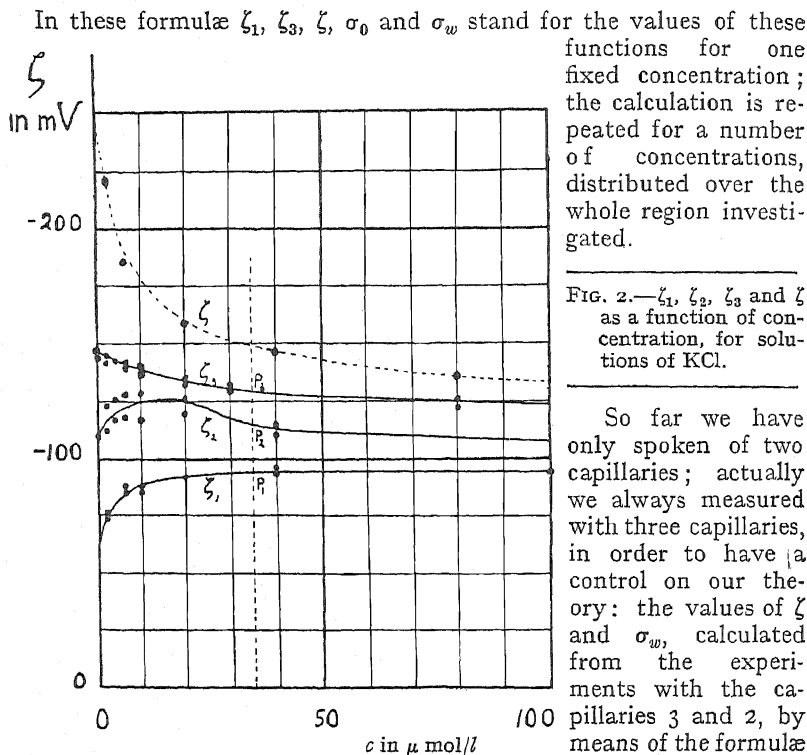
The true value of  $\zeta$  may be obtained from these curves in the following way: at the points  $P_1$  and  $P_3$   $\zeta$  will have the same value; the same holds for  $\sigma_w$ ; therefore it follows from (10):

$$\zeta = \zeta_1 \left( 1 + \frac{2\sigma_w}{r_1\sigma_0} \right) = \zeta_3 \left( 1 + \frac{2\sigma_w}{r_3\sigma_0} \right) \quad (13)$$

or 
$$\sigma_w = \frac{\frac{\zeta_3 - \zeta_1}{\zeta_1} \sigma_0}{\frac{\zeta_1}{r_1} - \frac{\zeta_3}{r_3}} \quad (14)$$

and 
$$\zeta = \zeta_3 \zeta_1 \frac{r_1 - \frac{1}{\frac{\zeta_1}{r_1} - \frac{\zeta_3}{r_3}}}{r_1} \quad (15)$$

<sup>7</sup> J. J. Bikerman, *Koll. Z.*, 1935, **72**, 100.



$$\sigma_w = \frac{\zeta_3 - \zeta_2}{\frac{\zeta_2}{r_2} - \frac{\zeta_3}{r_3}} \frac{\sigma_0}{2} \quad (14')$$

and

$$\zeta = \zeta_3 \zeta_2 \frac{\frac{1}{r_2} - \frac{1}{r_3}}{\frac{\zeta_2}{r_2} - \frac{\zeta_3}{r_3}} \quad (15')$$

must, of course, agree with the values calculated from the experiments with capillaries 3 and 1.

## 2.

Preliminary experiments, done in collaboration with Mr. Verlende and Miss Moorkens<sup>a</sup> gave results, already represented in Fig. 2. These results were obtained with solutions of KCl of concentrations from 0.80  $\mu$  mol./l. The pure water had a specific conductivity in these experiments of  $6.8 \times 10^{-7}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, i.e. it still contained a few  $\mu$  mols. of impurities. Constant pressure was given with help of the apparatus shown schematically in Fig. 3; for further details of the apparatus we refer to the communication just quoted. From Fig. 2 it is seen that the true value of  $\zeta$  at  $c = 0$  amounts to  $-230$  mV, which is totally different from the values  $\zeta_1$  ( $-70$  mV),  $\zeta_2$  ( $-110$  mV) and  $\zeta_3$  ( $-140$  mV), obtained with capillaries of radii  $r_1 = 0.011$  cm.,  $r_2 = 0.025$  cm. and  $r_3 = 0.039$  cm.

<sup>a</sup> A. J. Rutgers, Ed. Verlende and M<sup>o</sup> Moorkens, *Proc. Kon. Akad. v. Wetensch. Amsterdam*, 1938, 41, 763.

In Table I we have collected all the data obtained with capillaries 1 and 3, at concentrations of 2, 6, 20, 40 and 80  $\mu$  mol./l.

TABLE I.—VALUES OF  $\sigma_w(c)$ ,  $\zeta(c)$ ,  $l(c)$  AND  $d(c)$  FOR SOLUTIONS OF KCl.

$c$ in $\mu$ mol./l. ( $\times 10^{-8}$ ).	$\sigma_w$ in $\text{ohm}^{-1}\text{cm.}^{-1}$ ( $\times 10^{-8}$ ).	$\zeta_s$ .	$\zeta_l$ .	$\sigma_w$ in $\text{ohm}^{-1}$ ( $\times 10^{-8}$ ).	$\zeta$ in mV.	$l$ in e.s.u./cm. <sup>2</sup> .	$d$ in cm. ( $\times 10^{-6}$ ).
2	10.5	— 143	— 75	1.13	— 222	2040	2.3
6	16.3	— 139	— 85	1.04	— 184	1660	2.3
20	35.2	— 134	— 91	1.57	— 165	2090	1.7
40	57.5	— 127	— 94	1.79	— 147	2090	1.5
80	135	— 121	— 95	3.18	— 136	2340	1.2

We draw attention to the fact that the value of  $\sigma_w$  increases slowly with the concentration; for a concentration of  $500 \times 10^{-8}$  mol./l. we calculate by extrapolation a value of  $\sigma_w = 14 \times 10^{-8}$  ohm<sup>-1</sup>, in satisfactory agreement with McBain,<sup>9</sup> from whose results, obtained with an entirely different method, an extrapolated value of  $10 \times 10^{-8}$  ohm<sup>-1</sup> is calculated; on the other hand, White, Urban and van Atta<sup>10</sup> arrive at a value of only  $0.224 \times 10^{-8}$  ohm<sup>-1</sup> for this concentration. Our new experiments, carried out with a much improved apparatus, and starting from a much purer water ( $\sigma_0 = 2.9 \times 10^{-7}$  ohm<sup>-1</sup> cm.<sup>-1</sup>), have given the following two values of  $\sigma_w$  at 500  $\mu$  mol./l.: 9.8 and  $7.5 \times 10^{-8}$  ohm<sup>-1</sup> (Fig. 6, Table II).

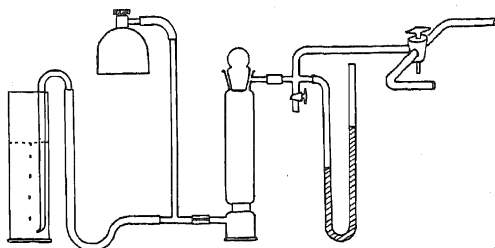


FIG. 3.

### 3.

Let us now compare the true  $\zeta$ -curve with theory.<sup>11</sup> From Poisson's equation

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{D} \quad (16)$$

and Boltzmann's equation

$$\rho = n_0\epsilon \left\{ \nu_+ z_+ e^{-\frac{z_+ e\psi}{kT}} - \nu_- z_- e^{\frac{z_- e\psi}{kT}} \right\} \quad (17)$$

(where we have assumed that the molecule of the electrolyte dissociates into  $\nu_+$  positive ions of charge ( $z_+e$ ) and  $\nu_-$  negative ions of charge ( $-z_-e$ ),  $\epsilon$  being equal to  $4.8 \times 10^{-10}$  e.s.u.) we have:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi n_0\epsilon}{D} \left\{ \nu_+ z_+ e^{-\frac{z_+ e\psi}{kT}} - \nu_- z_- e^{\frac{z_- e\psi}{kT}} \right\} \quad (18)$$

or 
$$2 \frac{d\psi}{dx} \frac{d^2\psi}{dx^2} = -\frac{8\pi n_0\epsilon}{D} \left\{ \nu_+ z_+ e^{-\frac{z_+ e\psi}{kT}} - \nu_- z_- e^{\frac{z_- e\psi}{kT}} \right\} \frac{d\psi}{dx} \quad (19)$$

<sup>9</sup> J. W. McBain, and colleagues, *J. Am. Chem. Soc.*, 1929, **51**, 3294; *J. Physic. Chem.*, 1930, **34**, 1033; 1935, **39**, 331.

<sup>10</sup> H. L. White, F. Urban and E. A. van Atta, *J. Physic. Chem.*, 1932, **36**, 3152.

<sup>11</sup> A. J. Rutgers and Ed. Verlende, *Proc. Kon. Akad. v. Wetensch. Amsterdam*, 1939, **42**, 71.

which, after integration, and introduction of the condition, that for

$x = \infty$   $\psi = 0$  and  $\frac{d\psi}{dx} = 0$ , gives:

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi n_0 kT}{D} \left\{ \nu_+ \left( e^{-\frac{z_+ e\psi}{kT}} - 1 \right) + \nu_- \left( e^{\frac{z_- e\psi}{kT}} - 1 \right) \right\} \quad (20)$$

The electric charge of the diffuse layer per cm.<sup>2</sup>,  $l$ , i.e., the charge, contained in a parallelopiped of 1 cm.<sup>2</sup> cross-section and extending in the liquid from  $x = 0$  to  $x = \infty$ , is equal to

$$l = \int_0^\infty \rho(x) dx = -\frac{D}{4\pi} \int_0^\infty \frac{d^2\psi}{dx^2} dx = \frac{D}{4\pi} \left( \frac{d\psi}{dx} \right)_0 \quad (21)$$

From (20) and (21) it follows ( $\psi(0) \equiv \zeta$ ):

$$l^2 = \frac{n_0 D kT}{2\pi} \left[ \nu_+ \left( e^{-\frac{z_+ e\zeta}{kT}} - 1 \right) + \nu_- \left( e^{\frac{z_- e\zeta}{kT}} - 1 \right) \right] \quad (22)$$

If we take into account that the values of  $\zeta$  run from  $-222$  to  $-136$  mV., it is clear that the term  $e^{-\frac{z_+ e\zeta}{kT}}$  in (22) is much larger than all the other terms, so that we may write:

$$l^2 \cong \frac{n_0 D kT \nu_+}{2\pi} e^{-\frac{z_+ e\zeta}{kT}} \quad (23)$$

or 
$$\zeta = \frac{kT}{z_+ e} \ln \frac{n_0 D kT \nu_+}{2\pi l^2} = \frac{0.058}{z_+} \log \frac{DRT \nu_+ c}{2000\pi l^2} \quad (24)$$

where  $c$  is the concentration of electrolyte in mol./l. At 25° C., and for our electrolytes ( $\nu_+ = 1$ ), we have:

$$\log \frac{DRT \nu_+}{2000\pi} = 8.50 \quad (25)$$

$$\zeta = \frac{58}{z_+} \times 8.50 + \frac{58}{z_+} \log c - \frac{116}{z_+} \log l = \frac{493}{z_+} - \frac{116}{z_+} \log l + \frac{58}{z_+} \log c \quad (26)$$

where  $\zeta$  is expressed in mV.

$$\log l = 4.25 - \frac{z_+ \zeta}{116} + \frac{1}{2} \log c \quad (27)$$

The values of  $l$  as a function of the concentration, calculated by means of this equation, will be found in Table I.

A value for the thickness,  $d$ , of the diffuse layer may be obtained with help of the formula for the capacity per cm.<sup>2</sup> of a flat condensator:

$$C = \frac{D}{4\pi d} = \frac{l}{-\zeta}$$

or 
$$d = -\frac{D\zeta}{4\pi l} \quad (28)$$

The same result is obtained in the following way (Gouy<sup>12</sup>): Let  $d$  be defined by

$$d = \frac{\int_0^\infty x \rho(x) dx}{\int_0^\infty \rho(x) dx} \quad (29)$$

<sup>12</sup> M. Gouy, *J. Physique*, (4°), 1910, 9, 457.

Now :

$$\int_0^{\infty} x \rho(x) dx = -\frac{D}{4\pi} \int_0^{\infty} x \frac{d^2 \psi}{dx^2} dx = -\frac{D}{4\pi} \left[ x \frac{d\psi}{dx} \right]_0^{\infty} + \frac{D}{4\pi} \int_0^{\infty} \frac{d\psi}{dx} dx = -\frac{D\zeta}{4\pi} \quad (30)$$

$$\int_0^{\infty} \rho(x) dx = l. \quad . \quad . \quad . \quad (31)$$

And thus 
$$d = -\frac{D\zeta}{4\pi l}. \quad . \quad . \quad . \quad (28)$$

The values of  $d$ , calculated by means of this formula, are also given in Table I. The charge  $l$  and the thickness  $d$ , both vary only slowly with concentration.

#### 4.

After the satisfactory results of the first experiments, a new apparatus was designed, half of which is shown diagrammatically in Fig. 4. A change

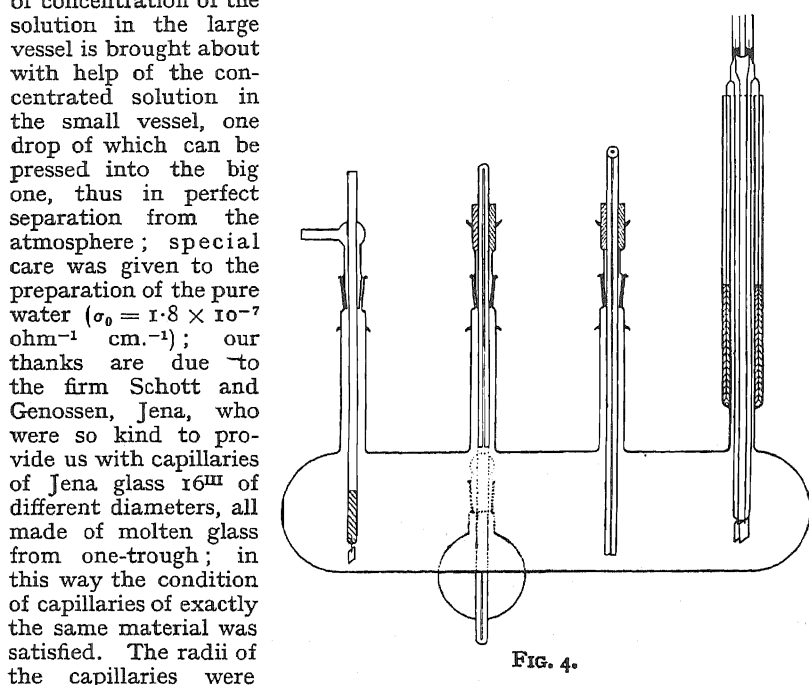


FIG. 4.

$r_1 = 0.01058$  cm.,  $r_2 = 0.02293$  cm.,  $r_3 = 0.03982$  cm.

Measurements with this apparatus were carried out by Mr. Verlande on solutions of KCl (0.400  $\mu$  mol./l., HCl (0.200  $\mu$  mol./l.,  $\text{CaCl}_2$  (0.100  $\mu$  mol./l. and  $\text{Al}(\text{NO}_3)_3$  (0.030  $\mu$  mol./l.). The temperature (KCl: 23.2° C., 24.8° C., 25.4° C.; HCl: 22.3° C., 22.4° C., 22.4° C.;  $\text{CaCl}_2$ : 22.8° C., 22.5° C., 22.5° C.) was during one series of measurements kept constant within a few tenths of a degree.

A survey of the results is given in Table II and III and Figs. 5-9; a more detailed account of these experiments will be given by Mr. Verlande and will be published elsewhere.

We draw attention to the good agreement between  $\zeta_{s,1}$  and  $\zeta_{2,1}$  in Table II (a), between  $\zeta_{s,1}$  and  $\zeta_{s,2}$  in Table II (b) and II (c); upon the anomalous kink in the  $\zeta_1$ ,  $\zeta_2$ ,  $\zeta_3$ -curves of HCl, and its explanation by the

## 76 STREAMING POTENTIALS AND SURFACE CONDUCTANCE

TABLE II.—VALUES OF  $\sigma_w(c)$ ,  $\zeta(c)$ ,  $l(c)$  AND  $d(c)$ .

$c$ in $\mu$ mol./l.	$\sigma_0$ in ohm <sup>-1</sup> cm. <sup>-1</sup> ( $\times 10^{-7}$ ).	$\zeta_1$ .	$\zeta_2$ .	$\zeta_3$ .	$(\sigma_w)^{3:1}$ in ohm <sup>-1</sup> ( $\times 10^{-8}$ ).	$(\sigma_w)^{2:1}$ in ohm <sup>-1</sup> ( $\times 10^{-8}$ ).	$\zeta_{3:1}$ in mV.	$\zeta_{2:1}^\dagger$ in mV.	$l_{2:1}$ in e.s.u./ cm. <sup>2</sup>	$d_{3:1}$ in cm. ( $\times 10^{-8}$ ).
0	2.9	-69	-110	-143	0.36	0.34	-236	-224	—	—
2	5.6	-83*	-127	-154	0.50	0.53	-223	-233	2090	2.24
6	10.8	-104	-144	-162	0.55	0.61	-203	-215	2450	1.74
10	16.0	-115	-150	-166*	0.61	0.65	-198	-203	2880	1.44
20	27	-127	-153	-164	0.70	0.72	-183	-186	3020	1.26
40	57	-128	-151	-157	1.01	1.19	-171	-178	3310	1.07
60	84	-128	-149	-156	1.44	1.57	-169	-173	3980	0.90
100	137	-128	-146	-153	2.08	2.16	-164	-166	4680	0.74
200	266	-122	-136	-147	4.2	3.3	-159	-151	5890	0.56
400	522	-117	-129	-139	7.6	5.8	-149	-141	6760	0.46

## A. Solutions of KCl.

0	2.9	-69	-110	-143	0.36	0.34	-236	-224	—	—
2	5.6	-83*	-127	-154	0.50	0.53	-223	-233	2090	2.24
6	10.8	-104	-144	-162	0.55	0.61	-203	-215	2450	1.74
10	16.0	-115	-150	-166*	0.61	0.65	-198	-203	2880	1.44
20	27	-127	-153	-164	0.70	0.72	-183	-186	3020	1.26
40	57	-128	-151	-157	1.01	1.19	-171	-178	3310	1.07
60	84	-128	-149	-156	1.44	1.57	-169	-173	3980	0.90
100	137	-128	-146	-153	2.08	2.16	-164	-166	4680	0.74
200	266	-122	-136	-147	4.2	3.3	-159	-151	5890	0.56
400	522	-117	-129	-139	7.6	5.8	-149	-141	6760	0.46

## B. Solutions of HCl.

0	2	-51	-97	-130	0.51	0.34	-296	-241	—	—
2	7	-115	-135	-148	0.16	0.21	-165	-170	660	5.2
6	22	-115	-119	-129	0.20	0.56	-135	-146	630	4.5
10	38	-106	-108	-116	0.27	0.85	-120	-129	600	4.2
20	78	-94	-98	-104	0.62	1.41	-108	-113	675	3.3
40	158	-88	-96	-99	1.49	1.41	-104	-103	890	2.5
60	238	-87	-95	-98	2.28	2.13	-104	-102	1100	2.0
100	394	-85	-94	-98	4.60	4.82	-104	-104	1410	1.5
150	507	-85	-94	-98	6.9	7.2	-104	-104	1740	1.3
200	780	-85	-94	-98	9.1	9.5	-104	-104	2000	1.1

C. Solutions of  $\text{CaCl}_2$ .\*

0	1.90	-57	—	-127	0.30	—	-229	—	—	—
0.5	3.21	-64	-102	-121	0.30	0.22	-178	-161	—	—
1	4.54	-69.3	-102	-118	0.31	0.25	-158	-150	—	—
1.5	5.80	-73.5	-102	-117	0.32	0.29	-149	-146	—	—
2.5	8.26	-80	-103	-115	0.31	0.31	-137	-137	—	—
5	14.20	-87	-104	-114	0.36	0.42	-128	-131	6900	0.39
10	25.85	-89.5	-100	-107	0.40	0.54	-115	-118	5600	0.43
20	37.70	-90	-98	-102	0.38	0.44	-107	-108	5000	0.45
25	61.55	-88.5	-95	-98	0.52	0.56	-102	-103	5400	0.40
50	118.9	-85.5	-88.5	-91	0.62	0.95	-93	-95	5300	0.37
75	174.1	-82	-84	-86	0.62	1.16	-88	-89	5000	0.36
100	229	-79	-81	-83.5	0.85	1.6	-85	-87	5400	0.33

\* The value of  $l$  (27) can only be calculated, if the concentration is known; therefore the first value of  $l$ , and consequently of  $d$  (28) is the one at a concentration of  $\text{CaCl}_2$  which is greater than the concentration of the impurities present.

†  $\zeta_{2:1}$  for KCl;  $\zeta_{3:2}$  for KCl and  $\text{CaCl}_2$ .

TABLE III.—VALUES OF  $\sigma_w(c)$  AND  $\zeta(c)$  FOR SOLUTIONS OF  $\text{Al}(\text{NO}_3)_3$ .

Conc. in $\mu$ mol./l	$\sigma_0$ in ohm <sup>-1</sup> cm. <sup>-1</sup> ( $\times 10^{-7}$ ).	$\zeta_1$ .	$\zeta_2$ .	$(\sigma_w)^{2:1}$ in ohm <sup>-1</sup> ( $\times 10^{-8}$ ).	$\zeta_{2:1}$ in mV.
0	2.25	-62	-104	0.35	-243
0.1	3.30	-69	-115	0.51	-268
0.2	4.00	-75	-125	0.61	-291
0.3	4.75	-76	-135	0.86	-403

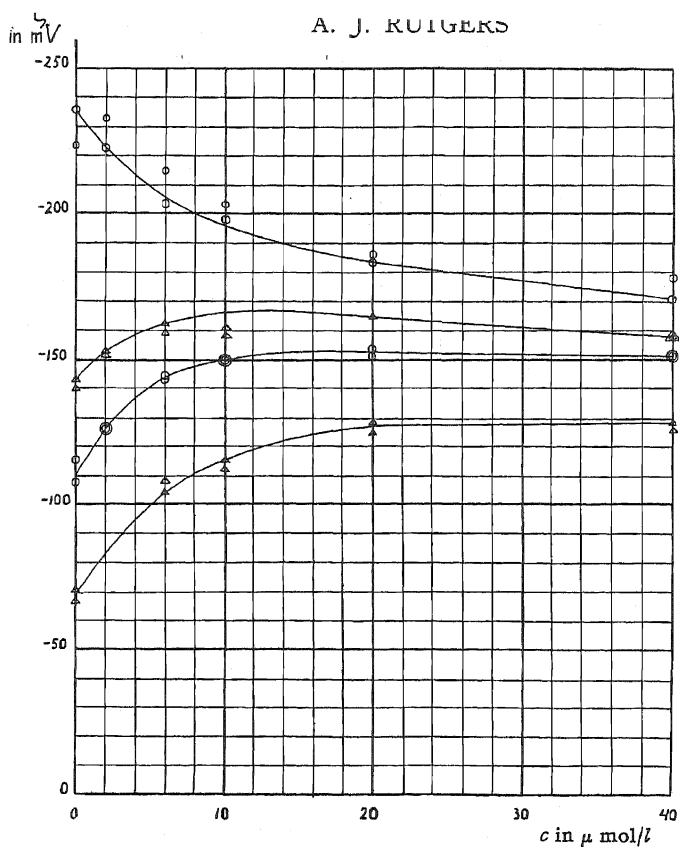


FIG. 5.— $\zeta_1$ ,  $\zeta_2$ ,  $\zeta_3$  and  $\zeta$  as a function of concentration for solutions of KCl.

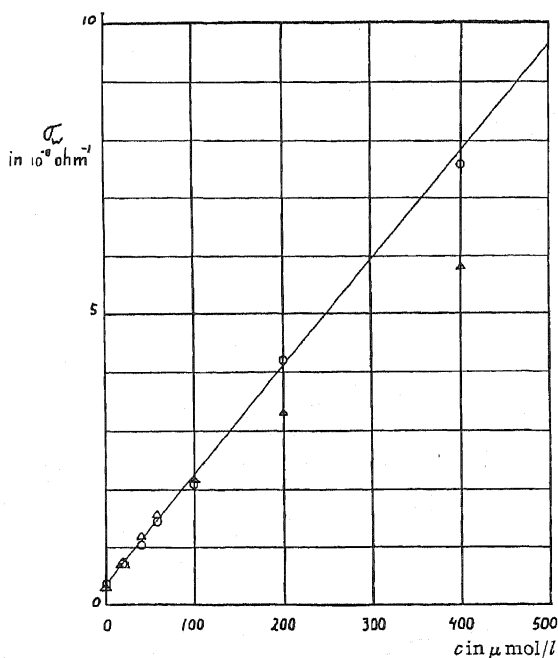


FIG. 6.— $\sigma_w$  as a function of concentration for solutions of KCl.

We draw attention to the fact that the anomaly in the  $\zeta_1$ , to  $\zeta_2$ ,  $\zeta_3$  curves at low concentrations is caused by an anomaly not of the  $\zeta$ -curve, but of the  $\sigma_w$ -curve.



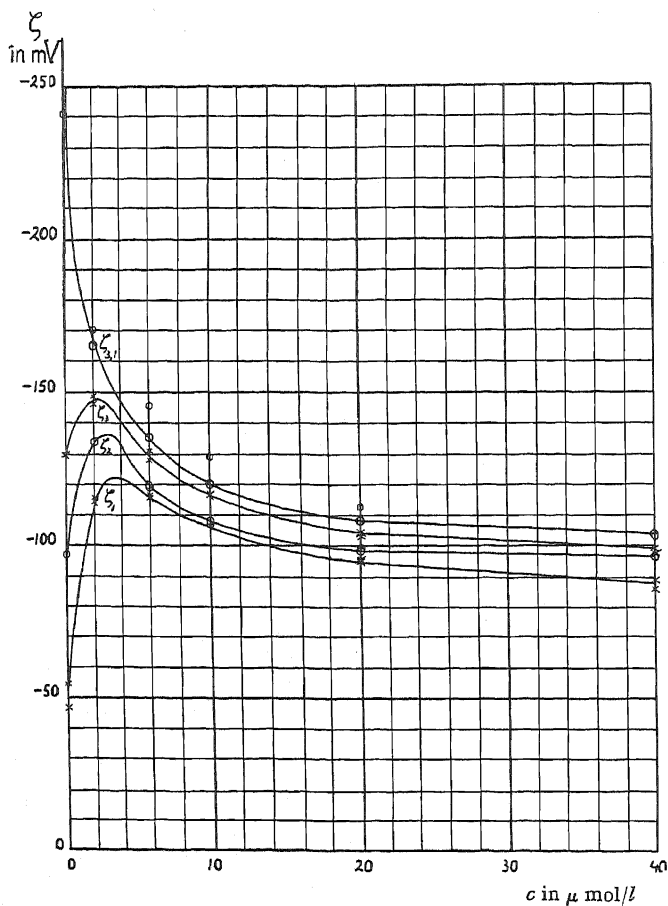


FIG. 7.— $\zeta_1(c)$ ,  $\zeta_2(c)$ ,  $\zeta_3(c)$  and  $\zeta(c)$  for solutions of HCl.

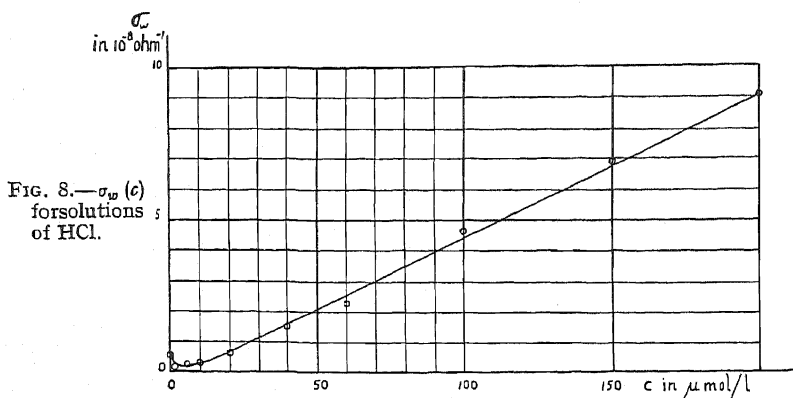


FIG. 8.— $\sigma_w(c)$  for solutions of HCl.

Measurements with solutions of  $\text{Al}(\text{NO}_3)_3$  are very difficult; at 0.30 or 0.50  $\mu\text{mol/l}$  the phenomena which lead to a change of the sign of the charge of the wall begin to manifest themselves; at higher concentrations the system very slowly reaches its state of equilibrium; the charge on the

wall changed already its sign in the third capillary while it did not yet in the first and the second; therefore only  $\zeta_{2,1}$  could be calculated;  $\zeta_{2,1}$  seems to increase with increasing concentration.

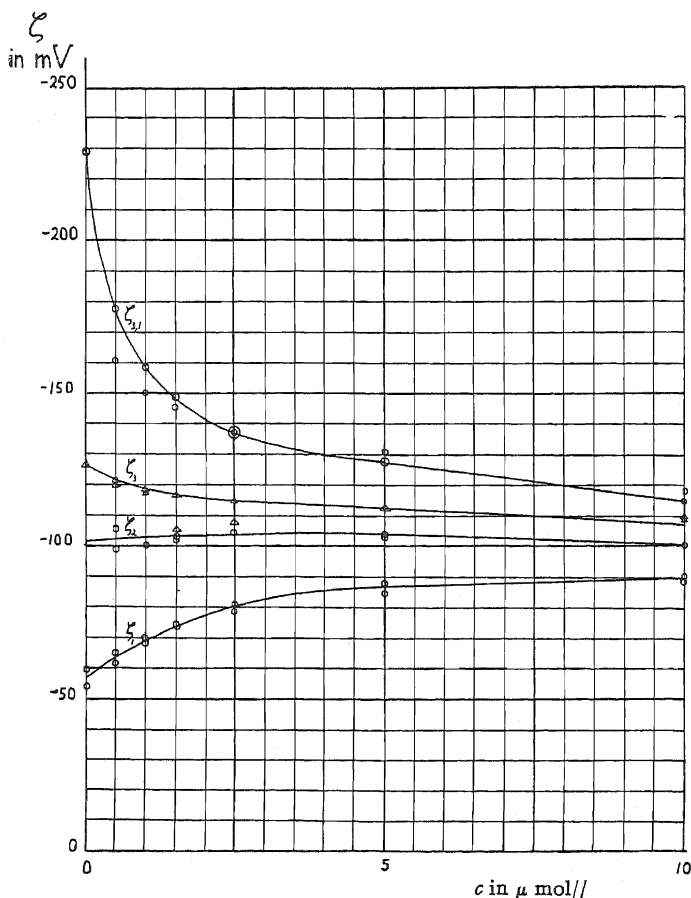


FIG. 9.— $\zeta_1$ ,  $\zeta_2$ ,  $\zeta_3$  and  $\zeta$  as a function of the concentration for solutions of  $\text{CaCl}_2$ .

### Summary.

1. The anomalous behaviour of the  $\zeta$ - $c$ -curve for solutions of KCl is attributed to surface conductance; derivation and correction of the equation of Helmholtz-Smoluchowski.

2. Survey of results obtained with the old apparatus.

3. Connection between  $\zeta$ ,  $l$  and  $c$  according to theory; calculation of the charge per  $\text{cm}^2$   $l$  and of the thickness of the double layer  $d$ .

4. Survey of results obtained with the new apparatus; measurements on solutions of KCl ( $0.400 \times 10^{-3}$  mol./l.), HCl ( $0.200 \times 10^{-3}$  mol./l.),  $\text{CaCl}_2$  ( $0.100 \times 10^{-3}$  mol./l.) and of  $\text{Al}(\text{NO}_3)_3$  ( $0.030 \times 10^{-3}$  mol./l.).

*Note added in Proof.*—From the values of  $l$ , and the mobilities of the ions, values of  $\sigma_w$  can be calculated; these values turn out to be many times smaller than the observed values ( $\sigma_w$ )<sub>3,1</sub>, the ratio being for KCl: 19, 30, and 48 at concentrations of 100, 200, and 400  $\mu$  mol./l.; for KCl:

15, 30, and 41 at concentrations of 40, 100, and 200  $\mu$  mol./l. From this we conclude that there are a great number of positive *and* negative ions in the neighbourhood of the wall; the positive charge  $l$  of the diffuse layer is brought about by a relatively small excess of positive ions; therefore other forces than purely electrostatic forces must play the main rôle in the neighbourhood of the wall.

If this picture of the constitution of the diffuse layer is supposed to represent also truly the diffuse layer surrounding a colloidal particle, the well-known discrepancy between observed and "calculated" conductivity of colloidal solutions can be explained.

## THE ELECTROVISCOUS EFFECT IN EGG ALBUMIN SOLUTIONS

BY HENRY B. BULL.

*Received 6th July, 1939.*

A minimum in the viscosity of protein solutions has generally been observed at the isoelectric point of the protein. This suggests that the electrostatic charge on the protein is important in increasing the viscosity on both the acid and basic sides of the isoelectric point.

As is well known, Smoluchowski<sup>1</sup> published an equation predicting an increase in viscosity of a suspension of spherical particles as a result of the electrostatic potential on the particles. This equation takes the form

$$\frac{\eta_s}{\phi} = 2.5 \left[ 1 + \frac{1}{\kappa \eta_0 a^2} \left( \frac{\zeta D}{2\pi} \right)^2 \right] \quad (1)$$

where  $\eta_s$  is the specific viscosity (specific viscosity is equal to the relative viscosity minus one),  $\phi$  is the volume of the suspended particles in 1 c.c. of the suspension,  $\kappa$  is the specific conductivity,  $a$  is the radius of the spherical particle,  $\eta_0$  is the viscosity of the pure dispersions medium,  $\zeta$  is the electrostatic potential on the particle, and  $D$  is the dielectric constant. Although a complete derivation of the equation was promised by Smoluchowski, it was never forthcoming.

More recently Krasny-Ergen<sup>2</sup> has considered this problem and has published a complete derivation of an equation for the electroviscous effect. His equation is identical with that of Smoluchowski's except that the numerical coefficient by which the term  $\left( \frac{\zeta D}{2\pi} \right)^2$  is to be multiplied has the value of 1.5 instead of 1.

Both Smoluchowski and Krasny-Ergen assume the suspended particles to be spherical in shape and the thickness of the double layer to be small as compared with the diameter of the particle. In general, neither of these assumptions are fulfilled by solutions of protein molecules. As Neurath<sup>3</sup> has pointed out, only two proteins so far studied have spherical

<sup>1</sup> M. v. Smoluchowski, *Koll. Z.*, 1916, 18, 194.

<sup>2</sup> W. Krasny-Ergen, *Koll. Z.*, 1936, 74, 172.

<sup>3</sup> H. Neurath, *Cold Spring Harbor Symposia on Quantitative Biology* (1938).

molecules. These are Bence-Jones  $\alpha$  and erythrocrucorin Arca. The asymmetry of egg albumin molecule is probably between 3 to 1 and 4 to 1 (the ratio of major and minor axes of an ellipsoid of revolution). As far as the thickness of the double layer is concerned it is probably greater than the diameter of most protein molecules except in fairly high electrolyte concentration. From these considerations it is therefore to be anticipated that neither the Smoluchowski nor the Krasny-Ergen equation would be valid for protein solutions. Nevertheless, it seems worth while to test these equations with experimental data.

The protein selected for this study was purified egg albumin. The viscosity of dilute solutions (less than 1 per cent.) of this protein was determined at 35° in an Ostwald type of viscosimeter. The  $pH$  was varied by the addition of the appropriate amounts of dilute NaOH or of HCl. The entire  $pH$  range was explored without the addition of electrolyte other than acid or base. The results shown in the upper curves of Fig. 1 were obtained. These experiments were then repeated except that the

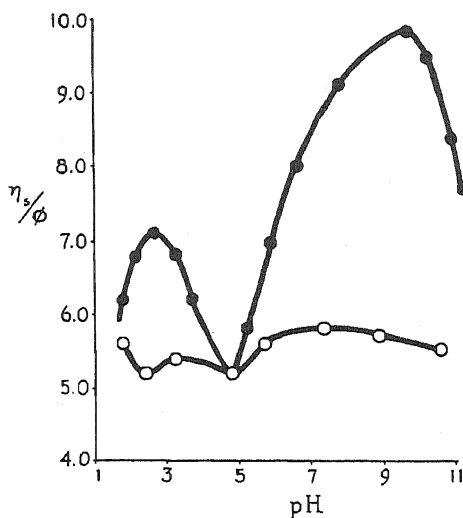


FIG. 1.—Shows the specific viscosity divided by the volume of egg albumin in 1 c.c. of solution ( $\eta_s/\phi$ ) as a function of  $pH$ . The upper curve (solid circles) is for solutions in the absence of NaCl; the lower curve (open circles) is for solutions in the presence of NaCl (0.01 N on basic side of isoelectric point and 0.02 N on the acid side).

solutions employed for the viscosity studies were 0.01 N in respect to NaCl on the basic side of the isoelectric point and 0.02 N in respect to this salt on the acid side. These results are shown in the lower curves in Fig. 1. The data shown in Fig. 1 indicate, qualitatively at any rate, a pronounced electroviscous effect which is largely suppressed by electrolytes.

The experimental details involved in the measurement of the viscosity will be published elsewhere. There was made, however, one rather remarkable observation which was so unexpected that it will be mentioned in this paper. When the times of outflow of a series of protein solutions of different concentrations, but at the same  $pH$ , were plotted against protein concentration a pronounced hiatus in the curve was often observed. Fig. 2 shows such a curve at the isoelectric point. This curious anomaly was studied in detail and the conditions for its appearance determined. In the calculation of the viscosity of protein solutions reported in this paper, cognizance was taken of this hiatus.

The conductivity of the protein solutions was measured at 35° C. on the same solutions which had been used for the viscosity determination.

Electrophoretic mobilities were determined in an Abramson micro-electrophoretic cell. They were done on quartz particles which had been coated with egg albumin by allowing the quartz particles to remain suspended in 0.4 per cent. egg albumin solution at least forty minutes before the measurements were made. The electrophoretic mobility of

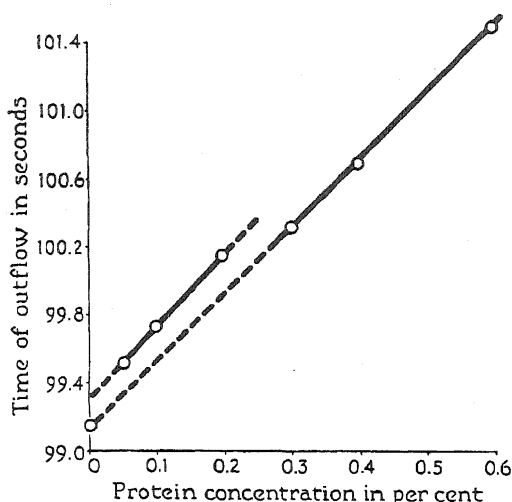


FIG. 2.—Shows time of outflow of egg albumin solutions at the isoelectric point as a function of protein concentration.

the protein adsorbed on quartz is probably not identical<sup>4</sup> with that of dissolved protein, but the mobilities of the two should not differ greatly and should in any case closely parallel one another. The mobility measurements were done at 28° C. and corrected to 35° C. They were made only on the basic side of the isoelectric point with and without the presence of 0.01 N NaCl.

The electrophoretic mobilities were squared and divided by the corresponding specific conductivity in reciprocal ohms. The factor so obtained was plotted against  $\eta_s/\phi$  for the protein solutions at the corresponding  $pH$  (Fig. 3). A smooth curve was drawn through the points. This smooth curve was thrown into the logarithm form by selecting a series of  $u^2/\kappa$  values from the curve which corresponds to the experimental  $\eta_s/\phi$  values and plotting the log

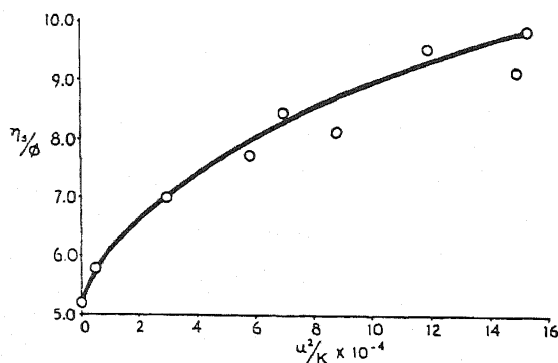


FIG. 3.—Shows the specific viscosity divided by the volume of egg albumin in 1 c.c. of solution ( $\eta_s/\phi$ ) as a function of the electrophoretic mobility of the protein squared and divided by the specific conductivity.

$\eta_s/\phi$  against the  $\log u^2/\kappa$  (Fig. 4). These points fell on a good straight line and allowed the evaluation of the coefficient and exponent of the function connecting  $\eta_s/\phi$  and  $u^2/\kappa$ . It turns out that the relation between these factors is

$$(\eta_s/\phi)_{\text{electrical}} = 0.00725 (u^2/\kappa)^{0.54} \quad (2)$$

<sup>4</sup> L. S. Moyer, *J. Physic. Chem.*, 1938, 42, 71.

This equation was tested by substituting the experimental values of  $u^2/\kappa$  and calculating the increase of viscosity of egg albumin solution due to the electroviscous effect. These values of  $(\eta_s/\phi)_{\text{electrical}}$  were then added to the viscosity at the isoelectric point and are shown in Fig. 5, plotted against  $pH$ . The experimental values of  $\eta_s/\phi$  are also

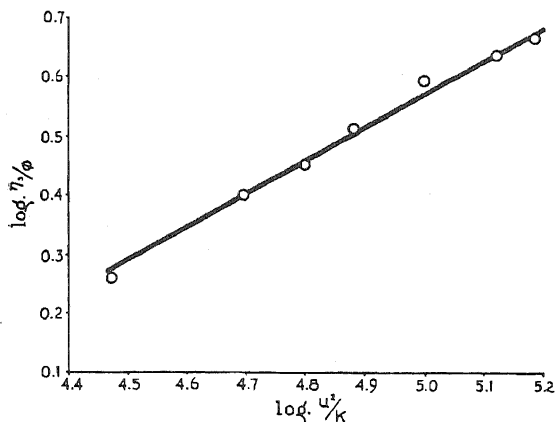


FIG. 4.—Shows the logarithm of the specific viscosity divided by the volume of egg albumin in 1 c.c. of solution ( $\log \eta_s/\phi$ ) as a function of the logarithm of the electrophoretic mobility squared and divided by the specific conductivity ( $\log u^2/K$ ).

shown in Fig. 5. The agreement between the calculated and the experimental is, by and large, good.

In Fig 4, if the slope of the line be changed slightly to make the exponent 0.5 instead of 0.54, then the empirical equation for the electro-viscous effect becomes

$$(\eta_s/\phi)_{\text{electrical}} = 0.0112 \frac{u}{\sqrt{\kappa}} \quad (3)$$

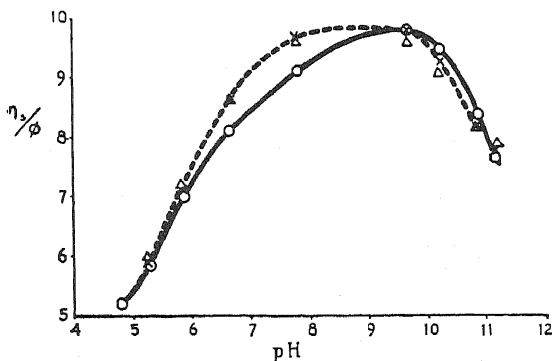


FIG. 5.—Shows  $\eta_s/\phi$  for egg albumin solutions in the absence of NaCl as a function of  $pH$ . Circles connected by continuous curve are the observed values. Triangles connected by broken curve are the values predicted by empirical equation 2. The crosses show the values predicted by empirical equation 3.

The experimental values for  $u$  and  $\kappa$  were substituted in this equation and  $\eta_s/\phi$  calculated. These are likewise shown in Fig. 5. It will be noted that the agreement between the calculated and experimental points is almost as satisfactory as that obtained with an exponent of 0.54. Since equation (3) is in a simpler form than equation (2), it will be assumed to be the correct expression.

The question arises as to how accurately does the Smoluchowski or the Krasny-Ergen equation predict the viscosity of egg albumin solutions. Before an actual test of these equations could be made the numerical

coefficient of 2.5 in the front of the brackets on the right-hand side of the equations had to be changed to 5.2. This was necessary because at the isoelectric point (absence of electroviscous effect)  $\eta_s/\phi$  is equal to 5.2 and not to 2.5. The test of these equations after this change had been made is shown in Table I (correction factors were applied to convert the potential and the conductivity to E.S.U. The zeta potential was calculated according to the equation

$$\zeta = \frac{6\pi\eta u}{D}$$

TABLE I.—OBSERVED AND CALCULATED VALUES OF  $\eta_s/\phi$   
( $a = 24.4$  Å units,  $D = 75$ ,  $\eta_0 = 0.0072$ ).

$\mu$ .	Observed.	Smoluchowski.	Krasny-Ergen.	Empirical Eq. 3.
<i>Without NaCl.</i>				
5.25	5.8	44.0	65.0	6.0
5.85	7.0	173.0	259.0	7.2
6.62	8.1	363.0	548.0	8.6
7.79	9.1	627.0	939.0	9.6
9.65	9.8	870.0	1303.0	9.6
10.20	9.5	756.0	1331.0	9.1
10.85	8.4	430.0	650.0	8.2
11.16	7.7	285.0	429.0	7.9
<i>With 0.01 N NaCl.</i>				
5.71	5.6	14.8	19.6	5.5
7.38	5.8	30.0	42.5	6.1
8.82	5.7	74.2	108.7	6.4
10.60	5.5	65.7	96.0	6.2

It can be seen from Table I that neither the Smoluchowski nor the Krasny-Ergen equations give the right order of magnitude for the electroviscous effect. The Smoluchowski equation gives values as high as ninety times that observed, while the Krasny-Ergen equation gives still higher values.

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# PART I.—(C) ELECTROCAPILLARITY AND OTHER METHODS.

## ON THE ELECTROCHEMISTRY OF SIMPLE INTERPHASES, WITH SPECIAL REFERENCE TO THAT BETWEEN MERCURY AND SOLUTIONS OF ELECTROLYTES.

By S. R. CRAXFORD.

Received 18th July, 1939.

The majority of previous work on the electro-chemistry of interphases has been concerned with three types, (i) the non-polarisable, and (ii) the polarisable interphase between a metal and a solution of an electrolyte, and (iii) the interphase between solutions of electrolytes and a non-conductor like air. And although this paper will be confined to a discussion of these types the conclusions drawn may readily be applied where necessary to other special kinds of interphases. For a theoretical treatment, the first two types have to be idealised as: (ia) the completely non-polarisable interphase whose potential is independent of the amount of charge flowed across it, and (iia) the completely polarisable interphase which behaves as if it contained a boundary that no charged particle can cross. These restrictions involve little loss in generality because the interphases met with in practice usually approximate well to the idealised types, as will be shown later.

In the first place it is necessary to adopt a system of nomenclature capable of describing the interphases accurately, and an extremely suitable one can be based on a paper of Lange and Miščenko<sup>1</sup> as follows.

When the double layer at the interphase has the form I the resulting potential difference between the phases is defined as the Volta potential difference,  $\Delta\psi$ . And since the solution side of the interphase contains ions that would not normally be present if the solution extended

Metal.	Solution.		Metal.	Solution.
—	Na +	Or	+	Cl —
—	Na +		+	Cl —
—	Na +		+	Cl —

I.

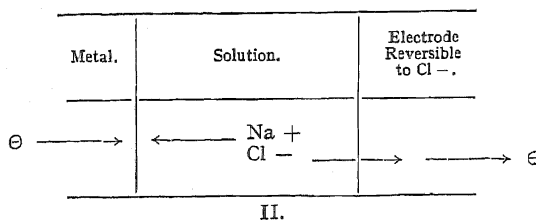
uniformly up to the phase boundary, there is adsorption of ions at the interphase and this is defined as the Volta adsorption,  $\Gamma_{Na+}^v$  or  $\Gamma_{Cl-}^v$ . Then if  $e$  is the charge on the solution side of the interphase and  $z_i$  the valency of the ion adsorbed,

$$e = z_i F \Gamma_i^v \quad (I)$$

<sup>1</sup> E. Lange and K. P. Miščenko, *Z. physikal. Chem.*, A, 1930, 149, 1.

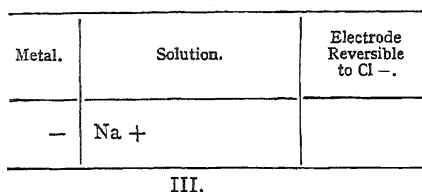


For a completely polarisable interphase such a double layer can only be



established by flowing charge on to the interphase from an external source, as II, giving III. If the charge moving in the external circuit is  $q$ , and the area of the interphase is  $s$ , the charge per unit area is therefore

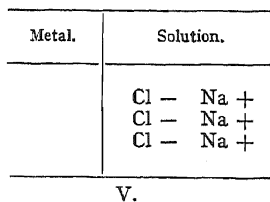
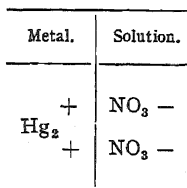
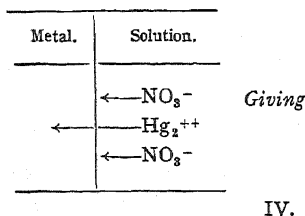
$$\epsilon = \left( \frac{\partial q}{\partial s} \right) \text{ Potential difference} \quad (2)$$



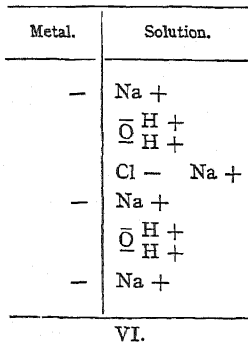
For a non-polarisable interphase the Volta layer is set up as in IV, without flow of current externally. And finally, for a solution

air interphase such layers cannot exist because ions from the solution are not soluble in the insulating phase.

When the interphase has the structure V the adsorption of the



sodium chloride is defined as specific adsorption,  $I_{\text{NaCl}}^s$ , and such adsorption is necessarily accompanied by a change in the potential difference between the phases, on account of the oriented ionic layers, and the potential difference due to this is called the specific adsorption potential,  $\chi_{\text{NaCl}}$ . Such layers are clearly set up without flow of external current, and can occur for all types of interphase. In the general case the distribution of ions in the interphase will be due to both Volta- and specific adsorption VI. The total potential difference between two points in the interior of the two phases is defined as the Galvani potential difference,  $\Delta\phi$ , and in the case shown



and in general

$$\Delta\phi = \Delta\psi + \chi_{\text{NaCl}} + \chi_{\text{H}_2\text{O}} + \chi_{\text{Metal}}$$

$$\Delta\phi = \Delta\psi + \Sigma\chi \quad (3)$$

## Results of a Thermodynamic Investigation of these Interphases.<sup>2, 3</sup>

(1) **The Non-Polarisable Interphase.**—The relation between the surface tension,  $\gamma$ , and the total adsorption is easy in this case, and is given by the usual Gibbs adsorption equation because the electrical factor introduces no additional degree of freedom. This is because when the interphase is expanded the potential difference is automatically kept constant by passage of particles across the interphase, and no external current flows. Hence if the suffix A denotes that the concentrations of all the components of the solution except the potential determining ion are kept constant, and if the activity of this latter ion is  $a_i$ ,

$$\left(\frac{\partial \gamma}{\partial \ln a_i}\right)_A = -\Gamma_i \frac{1}{RT}, \quad (4)$$

and further, since 
$$\left(\frac{\partial \Delta \phi}{\partial \ln a_i}\right)_A = \frac{RT}{z_i F}, \quad (5)$$

it follows that 
$$\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_A = -z_i F \Gamma_i. \quad (6)$$

If it is further assumed that specific adsorption of the potential determining ion is zero, then  $\Gamma_i = \Gamma_i^v$ , and

$$\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_A = -\epsilon. \quad (7)$$

(2) **The Completely Polarisable Interphase.**—The most important relationship for this interphase is the Lippman equation,

$$\left[\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_s = -\left(\frac{\partial q}{\partial s}\right)_{\Delta \phi} = -\epsilon\right]_C \quad (8)$$

where the suffix C denotes constant composition of the solution. This equation holds whether specific adsorption is occurring or not, and is perfectly general, a point which is by no means universally recognised. In the absence of specific adsorption the variation of the electrocapillary curve with the concentration of any ionic component  $i$  in the solution is given by

$$\left(\frac{\partial \gamma}{\partial \ln a_i}\right)_A = -\Gamma_i^v \cdot \frac{1}{RT}, \quad (9)$$

but a more useful form of this expression is obtained by combining it with (1) and (8), and is

$$\left(\frac{\partial \Delta \phi}{\partial \ln a_i}\right)_{A, \gamma} = \frac{RT}{z_i F}. \quad (10)$$

In the presence of specific salt adsorption,  $\Gamma_i^v$  in (9) becomes  $(\Gamma_i^s + \Gamma_i^v)$  and the final equation is less simple but shows that the displacement of the curves along the potential axis is greater than when the specific adsorption is zero. At the electrocapillary maximum, where  $\Gamma^v = 0$ , and  $\Gamma = \Gamma^s$ , the equation (9) becomes

$$\left(\frac{\partial \gamma^{\max.}}{\partial \ln a_i}\right)_A = -(\Gamma_i^s)^{\max.} \frac{1}{RT}. \quad (11)$$

<sup>2</sup> S. R. Craxford, O. Gatty, J. St. L. Philpot and H. A. C. McKay, *Phil. Mag.*, (7), 1933, 16, 849; 1934, 17, 54; 1935, 19, 965; 1936, 22, 359.

<sup>3</sup> F. O. Koenig, *J. Physic. Chem.*, 1934, 38, 111, 339.

and enables the amount of specific salt adsorption at the maximum to be calculated. Since there is no Volta adsorption the interphase is as in

Metal.	Solution.
	Cl — Na +
	Cl — Na +
	Cl — Na +
VII.	

VII, and since the potential difference across the double layer of salt is known from the displacement of the potential of the electrocapillary maximum from its value in pure water, the expression

$$K^s = \frac{F(\Gamma^s)_{\max.}}{\chi} \quad (12)$$

may be obtained, and may formally be called the electrostatic specific adsorption capacity, which is to be compared and contrasted with the ordinary electrostatic capacity of the Volta layer, which is obtained by differentiating equation (8) with respect to potential.

**(3) The Air-Solution Interphase.**—This is exactly equivalent to the case of the electrocapillary maximum, since specific adsorption only can occur. The only equations therefore that apply to it are (11) and (12). Equation (8) can never be usefully applied to such interphases because in the absence of Volta adsorption it reduces to  $0 = 0$ .

**Theories of the Detailed Structure of the Interphase.**—As early as 1879 v. Helmholtz considered that the ions carrying the net charge on the solution side of the interphase will be in contact with the metal surface, and that the equal and opposite charges on the other side of the interphase will be in the metal surface. This picture is idealised by taking the charge on the solution side to be evenly distributed over a plane at a distance  $\delta$  from the metal surface,  $\delta$  being the ionic radius, and thus the interphase becomes equivalent to a parallel plate condenser, whose charge  $\epsilon$  and capacity  $K$  per unit area are given by

$$K = \frac{\epsilon}{\Delta\phi} = \frac{1}{4\pi\delta} \quad (13)$$

This equation has been attacked on the ground that if the experimental value of about 20 microfarads is inserted for the capacity, the value of  $\delta$  comes out to be impossibly small. But this objection is overcome, and at the same time the formula can be brought up to date by putting in the dielectric constant  $D$  of the ions, because it is clear that the ions forming the solution side of the double layer are themselves polarisable and must not be treated as point charges separated from the metal by a vacuum. It is usual nowadays to consider that the equal and opposite charges in the metal are not on the surface, but are mirror image charges in the surface, so that  $\delta$  should be replaced by the ionic diameter  $d$ , and the capacity is then given by

$$K = \frac{\epsilon}{\Delta\phi} = \frac{D}{4\pi d} \quad (14)$$

A more fundamental criticism of this theory is that raised by Gouy,<sup>4</sup> who pointed out that in neglecting the effect of thermal agitation which

\* Professor Rideal has emphasised that this assumption of the parallel plate condenser leads directly to the Lippmann equation without any other assumption such as that of complete polarisability. Because the energy of such a condenser is  $2\pi d\epsilon^2/D$ , and hence

$$\left(\frac{\partial\gamma}{\partial\Delta\phi}\right)_c = -\frac{\partial(2\pi d\epsilon^2/D)}{\partial\Delta\phi} = -\epsilon.$$

<sup>4</sup>G. Gouy, *Ann. Physique*, 1917, (9), 7, 129.

tends to destroy the uniform arrangement of the ions in v. Helmholtz' double layer, equations (13) and (14) if applied to the general case contravene the second law of thermodynamics, and make  $\epsilon$  a function of  $\Delta\phi$  independent of the temperature and concentration of the solution, which is contrary also to experiment. Gouy,<sup>5</sup> and independently, Chapman,<sup>6</sup> considered the effect of the thermal agitation in making the double layer have a more diffuse character, and obtained the following equation:

$$\epsilon = \sqrt{\frac{D_w RT}{2\pi}} c \left( e^{F\Delta\phi/2RT} - e^{-F\Delta\phi/2RT} \right), \quad (15)$$

where  $D_w$  is the bulk dielectric constant of the solvent and  $c$  is the concentration of the electrolyte in the solution. This equation, however, is of even more limited application than the v. Helmholtz one, because it gives capacities of the order of 250 microfarads instead of about 20, and also gives the impossible result that the majority of the ions forming the solution side of the double layer are nearer to the surface than  $10^{-8}$  cm. This has come about because Gouy considered the ions as point charges and integrated  $\int \sigma d\phi$  ( $\sigma$  is the charge density) from the bulk of the solution right up to the metal surface. He should have integrated from the bulk up to an ionic radius from the metal surface, but he could not do so because the potential at such a distance from the surface is unknown. Stern<sup>7</sup> got over this difficulty by assuming that the number of ions in immediate contact with the metal is given by Langmuir's adsorption equation, and that the outer part of the double layer is accounted for by Gouy's theory. In this way he obtained the following equation for uni-univalent electrolytes.

$$\begin{aligned} \epsilon &= \frac{K}{1\Delta^2\phi} = K^4(1\Delta^2\phi - 4\Delta^2\phi) = \frac{D}{4\pi a}(1\Delta^2\phi - 4\Delta^2\phi) \\ &= F \cdot N_A \left( \frac{1}{2 + \frac{1}{\nu} e^{\frac{\phi_- - F^4\Delta^2\phi}{RT}}} - \frac{1}{2 + \frac{1}{\nu} e^{\frac{\phi_+ + F^4\Delta^2\phi}{RT}}} \right) \\ &\quad + \sqrt{\frac{D_w RT}{2\pi(18)}} \left( e^{\frac{F^4\Delta^2\phi}{2RT}} - e^{-\frac{F^4\Delta^2\phi}{2RT}} \right) \end{aligned} \quad (16)$$

where  $K^4$  is the capacity of the metal and the first layer of adsorbed ions,  $4\Delta^2\phi$  is the potential difference between this adsorbed layer and the bulk of the solution,  $1\Delta^2\phi$  is that between the metal and the bulk of the solution,  $N_A$  is the number of mols. adsorbed/cm.<sup>2</sup> in the adsorbed layer,  $\nu$  is the concentration of the solution expressed in molar fraction, and  $\Phi_i$  is the specific adsorption potential of an ion  $i$ . This equation corresponds to a distribution of charge in the double layer of either of the types indicated in Fig. 1, and it gives a charge—potential curve of the form of Fig. 2. At large positive or negative potentials the curve approaches a straight line of slope given by equation (14). As the concentration is decreased these straight lines move along the potential axis at a rate identical with the thermodynamical equation (10). At very small potentials and particularly also at small concentrations Stern's equation approximates to that of Gouy.

<sup>5</sup> G. Gouy, *C.r.*, 1909, 149, 654.

<sup>6</sup> D. L. Chapman, *Phil. Mag.*, 1913, 25, 475.

<sup>7</sup> O. Stern, *Z. Elektrochem.*, 1924, 30, 508.

Stern's theory is also important in that it is the first theory to bring the electrokinetic charge and potential into relationship with the other static properties of the interphase already described. When there is relative motion between a solid phase and a solution of an electrolyte, the solid will have a certain number of ions of the electrolyte firmly attached to it, and the plane of slip between these ions and the rest of the solution is in effect the phase boundary for all electrokinetic measurements. The charge obtained from such measurements is only the net charge on either side of this slip plane, and it has no direct connexion with the total charge or the total ionic adsorption at the interphase, because these latter are measured with respect to more fundamental boundaries and are properties of the static interphase. The same applies to the electrokinetic potential  $\zeta$ , which is merely the difference of potential between the slip plane and the bulk of the solution. Stern

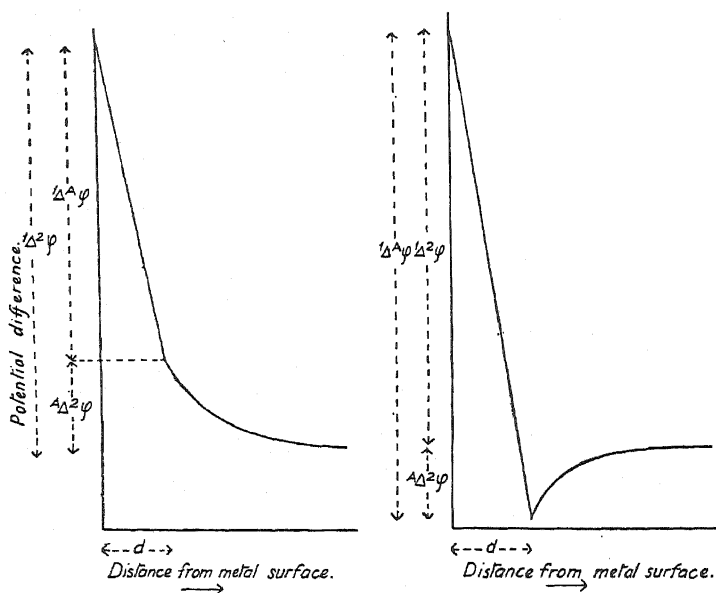


FIG. 1.—Stern's theory of the double layer.

now assumes, and reasonably so, that the slip plane will occur between the adsorbed and diffuse parts of the double layer, and hence that  $\zeta = \Delta^2\phi$  in equation (16). This theory shows why  $\zeta$  has so little apparent relationship with  $\Delta^1\phi$  and is normally so much smaller than it, and it also gives the result that the  $\zeta$ -concentration curve will contain a maximum or minimum.

**Applications to the Mercury—Solution Interphase.**—The interphase that has been most widely studied in the past on account of the very different experimental methods available for it, is that between mercury and solutions of electrolytes, but in spite of the large amount of experimental material available the chemistry of this relatively simple interphase is still disputed. From every point of view therefore, it seems best to consider the applications of the preceding theory to this system, and this will illustrate at the same time how it may be applied in other cases. In the first place it is necessary to consider under what conditions the mercury-solution interphase approximates to one or other of the ideal types of

interphase sufficiently closely for the derived equations to apply to it with accuracy.

(1) The interphase between mercury and a solution containing mercurous ions in relatively high concentration approximates to the completely non-polarisable type, since mercurous ions are common to both phases and can pass freely across the interphase. When current is flowed across the interphase it is carried by mercurous ions, and the potential

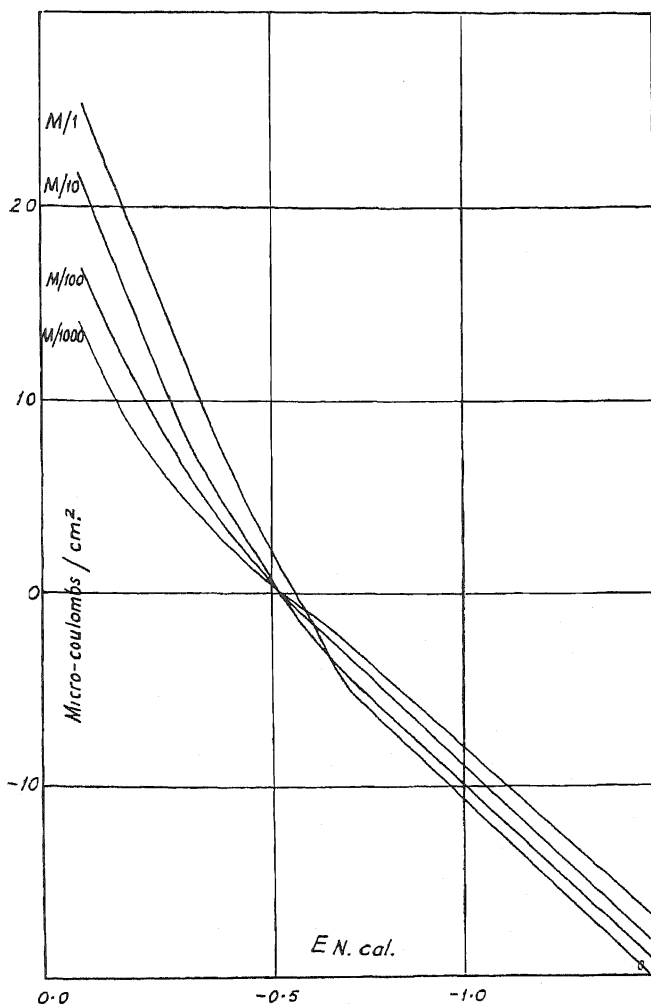


FIG. 2.—Charge-potential curves for solutions of sodium chloride.

difference between the phases will only remain unchanged if the concentration of mercurous ions in the layer of solution adjacent to the metal is also unchanged. In such a case the interphase will be completely non-polarisable. But in practice flow of current necessarily produces changes, by electrolysis, in the concentration of mercurous ions at the interphase so that the interphase will only approximate to the non-polarisable type if this electrolytic concentration change approximates to zero. The magnitude of this change is governed by two factors: (i) the magnitude of the current flowing through the interphase, and (ii) the reciprocal of

the concentration of the mercurous ions in the solution. Thus the introduction of  $10^{-4}$  g. of mercurous salt into the solution by electrolysis will have a negligible effect for solutions more concentrated than  $10^{-2}$  molar, but will have an increasingly large effect for more dilute solutions. Therefore for small currents or concentrated solutions of mercurous salt the interphase approximates to the non-polarisable type, but for large currents or dilute solutions it does not. The concentration of the most dilute solution consistent with a completely non-polarisable interphase decreases as the current that is flowed across the interphase decreases. These considerations agree with the results of Rosenberg and Stegeman,<sup>8</sup> confirmed by our own measurements, that whereas a stationary mercury—mercurous nitrate solution interphase behaves as non-polarisable in very dilute solutions, as for example in electrode potential measurements in which only very small currents flow across the interphase, yet the same interphase is only non-polarisable in solutions more concentrated than about M/10 for dropping electrode measurements in which a considerable current flows across the interphase.

(2) The interphase between mercury and a solution containing no mercurous ions approximates to the completely polarisable interphase over the potential range  $E_{N.Cal.} = 0.0$  to  $-1.3$  volt. From the definition of a completely polarisable interphase it follows that when such an interphase is polarised to any given potential difference by flowing charge onto it, and is then insulated, the potential difference and hence also the surface tension must remain unaltered. The interphase between mercury and a solution containing no mercurous ions does not, however, behave in this way, but the potential difference decays with time, more or less rapidly according to the conditions. This superimposed irreversible process resulting in the decay of the potential difference is always excessively slow compared with the rate at which the potential difference can be controlled by the polarisation process, because the former rate is that at which dischargeable ions or molecules can reach the interphase and become discharged there. Over the above mentioned potential range this rate is always slow, for either the dischargeable substance is only present in very small amounts, or its rate of discharge is kept low by a large overvoltage, or both. The rate of the polarisation process, on the other hand, is only governed by the electrical resistance of the circuit, and in the limit of zero resistance it becomes equal to the velocity of light. The truth of this argument is demonstrated by the behaviour of an ordinary capillary electrometer when the potential difference across the interphase is temporarily altered by displacing the meniscus from its resting position. When this is done with the external circuit closed the meniscus returns to its original position instantaneously, showing that the potential difference is restored to its original value very quickly by flow of charge round the circuit. When the external circuit is open, however, the meniscus only returns to its resting position very slowly, for now the only process available for the readjustment of the potential difference is the slow passage of charged particles across the interphase. Further, the magnitude of the depolarisation current in a capillary electrometer gives a direct measure of the irreversible electrolytic processes at the interphase, and this current is well known to be small, in fact  $10^{-3}$  to  $10^{-4}$  amp./cm.<sup>2</sup> Koenig<sup>9</sup> has also demonstrated that the electrocapillary curve for M/1 potassium nitrate solution is independent of the magnitude of the depolarisation current, provided that this is small, and that the curve for M/10 potassium nitrate solution is only very slightly dependent on it. On these grounds, therefore, it appears justifiable to neglect the inevitable but small irreversible electrolysis that occurs at the interphase between mercury and a solution

<sup>8</sup> J. E. Rosenberg and G. Stegeman, *J. Physic. Chem.*, 1926, 30, 1312.

<sup>9</sup> F. O. Koenig, *Z. physikal. Chem.*, A, 1931, 154, 421 and 454; *ibid.*, 1931, 157, 96.

containing no mercurous ions when it is polarised to potentials between  $E_{N. Cal.} = 0.0$  and  $-1.3$  volts, and to assume that the interphase approximates sufficiently closely to the completely polarisable type for the equations developed in the thermodynamic section of this paper to apply to it. That the most important of these equations, namely the Lippmann equation, does apply, is demonstrated later.

This treatment of the polarised mercury-solution interphase as a completely polarisable interphase is in accord with the earlier fundamental ideas on electrocapillarity of Lippmann,<sup>10</sup> v. Helmholtz,<sup>11</sup> and Planck,<sup>12</sup> but it is in direct contradiction to the concentration polarisation theory of Warburg,<sup>13</sup> Gibbs,<sup>14</sup> and Frumkin.<sup>15</sup> Because this latter theory has been accepted since its inception up to the present time, it is necessary to state briefly the reasons which lead to its final rejection. According to the theory of concentration polarisation there is always complete electrochemical equilibrium between the metal and the layer of solution nearest to it, so that if  $a'$  is the activity of mercurous ions in this layer, the equation

$$d\Delta\phi = \frac{RT}{2F} d \ln a'$$

always holds. For a system consisting of mercury in contact with a solution containing potassium nitrate at any concentration, and mercurous nitrate at an activity  $a$ , the initial potential difference is given by

$$d\Delta\phi_0 = \frac{RT}{2F} d \ln a,$$

but when the interphase is polarised by flowing current across it, mercurous ions will be removed from that part of the solution near the metal surface at a rate proportional to the current, and the resulting deficiency will be made good, in whole or in part, by diffusion from the bulk of the solution at a rate governed by Fick's law. Thus a steady state will be set up when these two rates become equal, and in this steady state the concentration of mercurous ions near the metal surface will, in general, be different from their concentration in the bulk of the solution. The potential across the interphase will therefore be given by the last equation but one,  $a'$  being the activity of mercurous ions near the metal in the steady state. Since  $\Delta\phi$  differs from the equilibrium potential  $\Delta\phi_0$  the electrode is polarised, and this type of polarisation is known as concentration polarisation. While there is no doubt that this theory is an approximation to the truth for small polarisations in cases where the solution contains much mercurous ion, there are the following reasons why it cannot possibly be applied to large polarisations and to systems in which the amount of mercurous salt in the solution is small.

(i) When the interphase is polarised to a potential of  $E_{N. Cal.} = -1.0$  volt, the concentration of mercurous ions near the mercury surface, as given by the above equation, is of the order of  $10^{-60}$ . The chemical potential of mercurous ions at this fantastically small concentration is clearly meaningless, on kinetic grounds, and cannot possibly be the determining factor for the behaviour of the interphase. This difficulty of the concentration polarisation theory of electrocapillarity has long been known, but attention has recently been refocussed on it by Andauer and Lange.<sup>16</sup>

(ii) If  $dq$  is the charge that has to be flowed in the external circuit in order to increase the potential difference by  $d\Delta\phi$ , then, in the case of con-

<sup>10</sup> G. Lippmann, *Ann. Chim. Physique*, 1875, (5), 5, 494.

<sup>11</sup> H. v. Helmholtz, *Wiss. Abhandl. physik. tech. Reichsanstalt*, 1879, 1, 925.

<sup>12</sup> M. Planck, *Ann. Physik*, 1891, 44, 413.

<sup>13</sup> E. Warburg, *Ann. Physik*, 1891, 41, 1.

<sup>14</sup> J. W. Gibbs, *Collected Works*, 1, 336, Longmans, Green & Co., New York.

<sup>15</sup> A. Frumkin, *Z. physikal. Chem.*, 1923, 103, 55.

<sup>16</sup> M. Andauer and E. Lange, *Z. physikal. Chem., A*, 1932, 162, 241.



centration polarisation,  $dq$  is the charge required to electrolyse mercurous salt into or out of the diffusion layer of the solution in order to change  $a$  by  $da$ . The diffusion layer is that wide layer of solution over which the activity of mercurous ions is varying from  $a$  to  $a'$ , and it is known that in such cases  $q$  is an exponential function of  $\Delta\phi$ . Thus an examination of the charge-potential curves in which  $q$  is plotted against  $\Delta\phi$  should show whether the polarisation is concentration polarisation or not. In Fig. 3 are shown a series of such curves taken from a paper by Erdey-Grúz and Kromrey,<sup>17</sup> who obtained them by a cathode ray oscillograph method for solutions of mercurous salts at various concentrations. For curve A, with  $c = 10^{-2}$ , the interphase is non-polarisable for the current used. For curve B, with  $c = 5 \times 10^{-5}$  the polarisation is typical concentration polarisation, but for smaller values of  $c$ , as in curves C and D, the polarisation clearly changes to a type in which  $q$  varies rectilinearly with

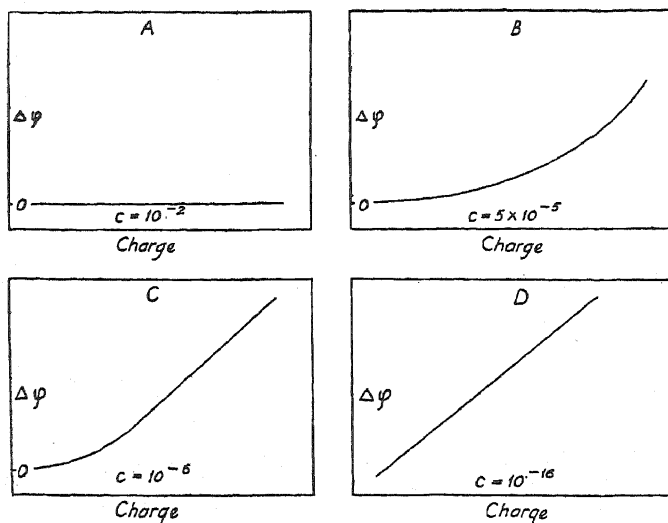


FIG. 3.—Charge-potential curves for solutions of mercurous nitrate from Erdey-Grúz and Kromrey.

$\Delta\phi$ . And it has already been shown that this is the form of curve to be expected if the interphase is completely polarisable.

(iii) The final piece of evidence is due to Samarcev,<sup>18</sup> who measured directly, by an interferometric method, the change of concentration produced near an electrode surface by flowing current across it. He found that even for quite small polarisations the observed concentration change is very much less than that predicted by the theory of concentration polarisation. If therefore the theory does not hold for such favourable cases, it will clearly not be obeyed at all for large polarisations and for solutions containing very little mercurous salt.

It is finally suggested that even if one or other of these arguments, taken alone, is not absolutely conclusive, nevertheless, when considered together, they form a strong case for the contention that under the given conditions of potential difference, the interphase between mercury and a solution containing no mercurous ions approximates closely to a completely polarisable interphase.

<sup>17</sup> T. Erdey-Grúz and G. G. Kromrey, *Z. physikal. Chem.*, A, 1931, 157, 213.

<sup>18</sup> A. G. Samarcev, *ibid.*, 1934, 168, 45.

### Experimental Data for the Mercury—Solution Interphase.

When considering the available experimental material in the light of the previous conclusions, it is well to give due weight at the beginning to the important paper of Proskurnin and Frumkin,<sup>19</sup> who showed that under normal experimental conditions these interphases are always contaminated, and that then their properties are very different from the properties of the clean interphases which can only be prepared and examined under very special conditions. The only data for the mercury—solution interphase obtained under such modern conditions of accuracy and cleanliness are those of (i) Proskurnin and Frumkin,<sup>19</sup> on the direct determination of  $\left(\frac{\partial q}{\partial \Delta \phi}\right)_s$ , and hence of the capacity; (ii) Philpot,<sup>20</sup> on the measurement of  $\left(\frac{\partial q}{\partial s}\right)_{\Delta \phi}$ , and hence also of the capacity, by the method of the dropping mercury electrode; and (iii) Koenig,<sup>9</sup> Hansen and Williams<sup>21</sup> and Craxford,<sup>22</sup> using a capillary electrometer. Details from the large mass of earlier work should be accepted with caution, although it is still of value in so far as it gives a general survey of the field. It is particularly to be regretted that the method of tabulation of Gouy's<sup>23</sup> comprehensive data precludes all chance of differentiating his curves, especially in view of the fact that the few data that he himself calculated for charge-potential curves appear to agree quite well with the more modern results. The position of all Gouy's curves on the  $E_{N, \text{cal.}}$  scale, and the relative position of one to another, are very uncertain because he only quotes data for this to 0.01 volt, and even this may be incorrect as he neglected liquid-liquid junction potentials entirely.

(1) **Comparison of  $\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_s$  and  $\left(\frac{\partial q}{\partial s}\right)_{\Delta \phi}$ .**—Frumkin<sup>15</sup> measured both these quantities directly in the same apparatus for one solution, and found good agreement for a series of potentials. He also compared the potential at which  $\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_s = 0$  with the potential where  $\left(\frac{\partial q}{\partial s}\right)_{\Delta \phi} = 0$  for a series of solutions and obtained good agreement even in cases where the electrocapillary curve is badly distorted by the adsorption of organic substances in the interphase. The most rigorous comparison, however, is that for a number of solutions of sodium and hydrogen chlorides in which the variation of  $\left(\frac{\partial q}{\partial s}\right)_{\Delta \phi}$  with  $\Delta \phi$  was measured by Philpot<sup>20</sup> by means of the dropping mercury electrode, and compared with the corresponding curves of  $\left(\frac{\partial \gamma}{\partial \Delta \phi}\right)_s$  against  $\Delta \phi$  obtained several years later in a capillary electrometer by Craxford.<sup>22</sup> The agreement shows the essential applicability of the Lippmann equation, (8), to this interphase.

(2) **The Negative Branch of the Charge—Potential Curve.**—For the potential range  $E_{N, \text{cal.}} = -0.8$  to  $-1.4$  volt the electrocapillary and charge-potential curves are particularly simple. The variation with concentration follows equation (10) strictly, for mono- di- and trivalent ions, showing, therefore, that the solution side of the double layer in this potential region contains these ions only adsorbed, and that there is no adsorption of negative ions. This result is specially important because the form of the electrocapillary and charge-potential curves is completely independent of the nature of the ion forming the solution side of the double layer,

<sup>19</sup> M. A. Proskurnin and A. Frumkin, *Trans. Faraday Soc.*, 1935, **31**, 110.

<sup>20</sup> J. St. L. Philpot, *Phil. Mag.*, (7), 1932, **13**, 775.

<sup>21</sup> L. A. Hansen and J. W. Williams, *J. Physic. Chem.*, 1935, **39**, 439.

<sup>22</sup> S. R. Craxford, *Dissert.*, Oxford, 1936.

<sup>23</sup> G. Gouy, *Ann. Chim. Physique*, 1903, (7), **29**, 145; 1906, (8), **8**, 291; 1906, (8), **9**, 75.

whether it is  $H^+$ ,  $K^+$ ,  $Ca^{++}$  or  $Al^{+++}$ , and if it were not for the concentration displacement result one might be inclined to explain this constancy of form by assuming that the ion forming the solution side of the interphase was  $H^+$  in all cases. The constant negative branch of the charge-potential curve is a straight line with a slope of  $19 \mu F./cm.^2$ , which gives the electrostatic capacity of the interphase in this region of potential. The constancy of the capacity whatever the cation is remarkable in view of the variation of the capacity when the solution side of the double layer consists of anions, and no satisfactory explanation has yet been given for it. But the linear form of the curve is in complete agreement with Stern's theory, which for relatively strong solutions and large charges degenerates into equation (14). Putting  $d = 2 \times 10^{-8}$  cm. and  $K = 19 \mu F./cm.^2$ , this equation gives  $D = 4.0$ . Such a value for the effective dielectric constant can be accounted for in two ways, firstly, because the ions forming the double layer are not point charges separated by a vacuum, but are themselves polarisable particles, so that for this reason alone  $D$  in equation (14) will be greater than unity. And in addition the lines of force between the two sides of the double layer will spread sideways from the individual ions and pass through neighbouring solvent molecules which will therefore contribute further to the dielectric constant (see Frumkin<sup>24</sup>). Finally, it should be mentioned that the number of ions so adsorbed at the interphase to form the solution side of the double layer is very small compared with the amount required to form a complete monomolecular layer. For sodium chloride, for example, this is about  $10^{18}$  ions/cm.<sup>2</sup>, whereas the number of sodium ions adsorbed for the double layer for a potential of 1.0 volt from the electrocapillary maximum is  $3.6 \times 10^{18}$ .

(3) **The Region of the Electrocapillary Maximum.**—The formal structure of the interphase in this region of potential has already been explained, and the following table (Craxford<sup>22</sup>) gives the numerical magnitudes of some of the quantities mentioned.

TABLE I.—THE ELECTROCAPILLARY MAXIMUM.

Electrolyte.	$\gamma_{max.}$ (Dynes/cm.).	$E_{N.Cal.}^{max.}$ (Volts).	$\chi_s$ (Volts).	$\Gamma_{max.}$ (Mols. $\times 10^{-10}$ .)	Specific Adsorption Capacity [ $K^2$ , $\mu F./cm.^2$ ].
KNO <sub>3</sub>	M/1	421.7	—0.56	0.04	0.9
	M/10	425.5	—0.525	0.005	
	M/100	426.5	—0.52	0.00	
	M/1000	426.5	—0.52	0.00	
NaCl	M/1	424.1	—0.56	0.04	0.5
	M/10	426.4	—0.525	0.005	
	M/100	426.8	—0.52	0.00	
	M/1000	426.8	—0.52	0.00	
KI	M/1	401.3	—0.82	0.30	3.1
	M/10	414.6	—0.73	0.21	
	M/100	422.7	—0.66	0.14	
	M/1000	425.3	—0.59	0.07	
CaBr <sub>2</sub>	M/2	416.2	—0.65	0.13	2.1
	M/20	423.3	—0.58	0.06	
	M/200	425.8	—0.54	0.02	
	M/2000	426.6	—0.52	0.00	

It should be noted in the first place that for this region of potential the charge potential curve is of a double exponential type in accordance with

<sup>24</sup> A. Frumkin, *Ergebnisse exakt. Naturw.*, 1928, 7, 235.

Stern's theory for small potential differences. Then, in very dilute solutions, whatever the nature of the electrolyte, the maximum surface tension is equal to 426.8 dynes/cm., which is the value for the interphase mercury-water. Hence no salt is adsorbed at the interphase at these maxima. For all cases where there is no specific salt adsorption at the maximum the potential of this maximum is approximately  $E_{N, \text{Cal.}} = -0.52$  volt, and for such cases the potential difference across the interphase is in general  $\Delta\phi = \chi_m + \chi_w$ , since  $\Delta\psi$  and  $\chi^*$  are zero. Of these  $\chi$ -potentials,  $\chi_m$ , the  $\chi$ -potential on the metal side of the interphase is always in the direction VIII and is understood qualitatively as arising on account of the kinetic energy of the metallic electrons, for when an electron approaches the surface of the metal it is carried some distance past the edge of the lattice of metallic positive ions before its direction of motion is reversed by the electric field. Values of  $\chi_m$  have been calculated by Sommerfeld,<sup>25</sup> and are of the order of several volts.  $\chi_w$ , the potential difference due to oriented water dipoles, on the solution side of the interphase, is unknown, but by analogy with the specific adsorption potential of salts, it is probably quite small.

Metal.	Solution.
+	-
+	+
+	-

VIII.

For solutions more concentrated than M/100 the maximum surface tension is in general different from 426.8 dynes/cm., and for the majority of electrolytes it is less, showing that there is specific salt adsorption at the maximum. The amount of this is shown in Table I, but it should be noted that in all cases it is very much less than the packed layer predicted theoretically by Gurney.<sup>26</sup> For these solutions the potential of the electrocapillary maximum is also displaced from its value in more dilute solutions, namely  $-0.52$  volt. In the majority of cases the displacement is towards the negative, showing that the specifically adsorbed salt is present in the

Metal.	Solution.
	I - K +
	I - K +
	I - K +

IX.

interphase in a film oriented in the direction shown in the diagram IX. This salt adsorption is due to specific interaction between the anions of the solution and the metallic mercury, and is not simply due to the two ions of the electrolyte being repelled out of the bulk of the solution to an unequal extent, because the  $\chi$ -potentials at the interphase solution-air, which are due to this latter cause, are very much smaller than the corresponding

$\chi$ -potentials at the mercury-solution interphase. This has been demonstrated by Frumkin.<sup>27</sup> Finally, the small values of the specific adsorption capacities of this layer of oriented adsorbed salt should be noticed, as they are distinctly smaller than the capacity of the Volta layer on the negative branch of the curve, and very much smaller than the corresponding capacities on the positive branch. This must mean that the effective separation of charge in the present case is greater than for Volta adsorption, and is probably not connected with a big distance between the layers of ions, as at X, but rather to a specific effect, as in XI, where the specific interaction between the nitrate ions and the mercury leaves the  $\ominus$  and the  $\text{K}^+$  ions as forming in effect the plates of the condenser.

(4) **The Positive Branch of the Curve.**—A consideration of that part of the electrocapillary and charge-potential curves which lies at potentials more positive than the electrocapillary maximum, shows that in general each positive branch consists of two sections. This distinction is clearest for the curve for M/1  $\text{KNO}_3$  solution, which is shown in Fig. 4.

<sup>25</sup> A. Sommerfeld, *Z. Physik*, 1928, 47, 1; *Naturwiss.*, 1928, 16, 374.

<sup>26</sup> R. W. Gurney, *Proc. Roy. Soc., A*, 1931, 134, 137.

<sup>27</sup> A. Frumkin, *Coll. Symp. Ann.*, 1929, 7, 89.

Metal.	Solution.
	$\text{NO}_3 - \text{K} +$
	$\text{NO}_3 - \text{K} +$
	$\leftarrow \text{---} \text{---} \text{---} \rightarrow$

Metal.	Solution.
	$\text{K}^+$  $\text{K}^+$

X.

XI.

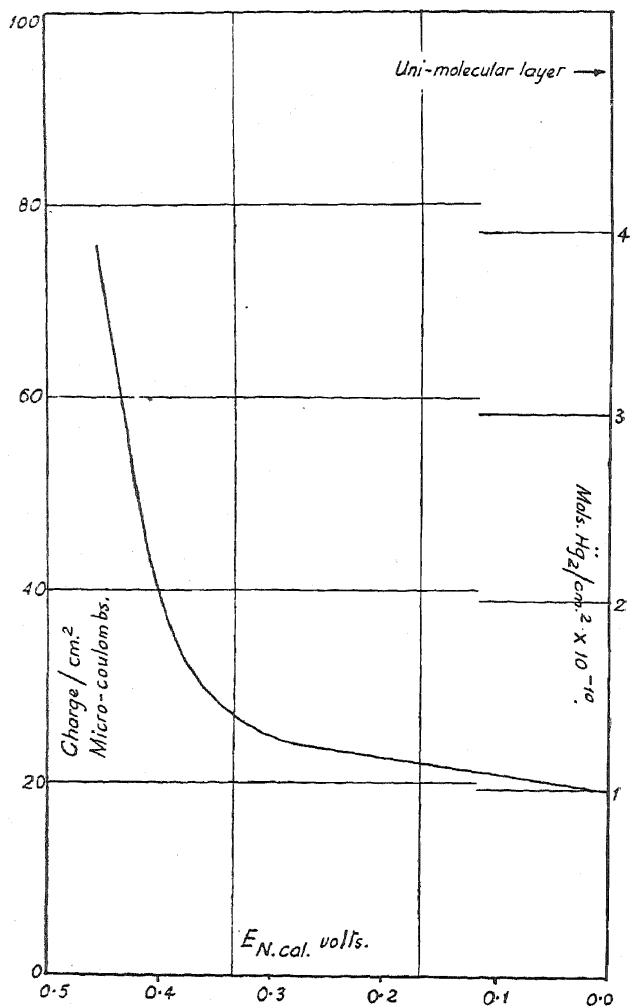
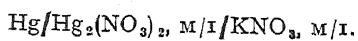


FIG. 4.—Charge-potential curve. M/1 potassium nitrate.

The positive limit of the curve is the discharging potential of the anion onto mercury, which in this case is the potential of the electrode



At this limit both the charge of the interphase and the capacity are very large. As the potential is made more negative both these quantities decrease exponentially, over a range of about 0.2 volt, and after this the charge-potential curve becomes rectilinear and the capacity constant. It is clear that the range of potential between the discharging potential of the anion and a point 0.2 volt more negative, embraces the transition between the completely polarisable and the non-polarisable types of interphase. An inspection of the corresponding electrocapillary curves shows that this region of potential is characterised by large salt adsorption at the interphase, and this section of the curve may conveniently be referred to as the transitional part of the positive branch. For several of the electrolytes examined, the distinction between the true and the transitional parts of the positive branch is not apparent from an inspection of the charge-potential curve, and in these cases the curve is judged by analogy to be of the transitional type if it is nearer the discharging potential of the anion than 0.2 volt, and also if there is excessive specific salt adsorption. Otherwise the curve is considered to be a true positive branch. Judged according to these standards the whole of the positive branches of the charge-potential curves for  $\text{KNO}_3$ , as normally obtained in a capillary electrometer, at concentrations from  $M/1$  to  $M/1000$ , for  $M/5$  sodium perchlorate, and for  $M/6$  to  $M/600$  aluminium sulphate solutions, for example, are all true positive curves. No part of the curves of potassium iodide or rhodanate, or calcium bromide can be considered to be true positive branches. The case of sodium chloride is more difficult because although the positive branch of the charge-potential curve for a  $M/1$  solution is rectilinear, it is doubtful whether the curve is a true positive branch, since so much of it is within 0.2 volt of the discharging potential of the chloride ions. For the more dilute solutions the curves are not rectilinear over much of their extent, but by taking their shape into consideration, the positive limit for the true positive branch may be put at  $E_{N.\text{Cal.}} = -0.3$  volt for the  $M/10$  solution,  $-0.25$  volt for  $M/100$ , and  $-0.2$  volt for the  $M/1000$  solution.

TABLE II.—CAPACITIES OF THE INTERPHASE. (Craxford.<sup>22</sup>)

Ion Forming Solution Side.	Concentration (Molar).	Capacity ( $\mu\text{F}/\text{cm}^2$ ).	
All +ve ions		19	
$\text{NO}_3^-$	1 — 0.001	24	} True +ve branch.
$\text{ClO}_4^-$	0.2	26	
$\text{SO}_4^{=}$	0.5 — 0.005	40	
$\text{Cl}^-$	1	43	
$\text{CNS}^-$	1	53	} Transitional +ve branch.
$\text{Br}^-$	1 — 0.001	93	
$\text{I}^-$	1 — 0.001	157	

From what has been said about the true positive branch of the curve it is clear that it is perfectly analogous to the negative branch, and that the structure of the interphase is that of a simple Volta layer, with little or no specific salt adsorption. Its capacity is given, therefore, by equation (14). Unlike the negative branch, where the capacity is independent of the nature of the cation forming the solution side of the interphase, here the capacities vary from anion to anion, and in all cases are rather larger than 19 microfarads, the value for the negative branch. This is not unexpected, because in spite of their larger size, anions are generally more deformable than cations, so that their centres of charge can approach the

metal surface more closely, and hence, by equation (14) have a larger capacity. The symmetrical and less deformable perchlorate ion has not a very high capacity, and neither has the nitrate ion, but the very deformable divalent sulphate ion has a capacity of 40.3 microfarads/cm.<sup>2</sup>.

(5) **The Transitional Positive Branch.**—If the interphase is assumed to be completely polarisable for this part of the curve, the connection between the large capacities and specific salt adsorption is simply explained, because if a given charge is put onto the interphase, the potential produced is not due to the distribution (XII), but is smaller on account of the specific adsorption, as shown at XIII.

Metal.	Solution.
+	I -
+	I -

XII.

Metal.	Solution.
+	I -
	I - K +
	I - K +
+	I -

XIII.

Although the capacities are not independent of the potential, the charge-potential curve is often not very different from a straight line, so that the values for the total capacity of the transitional part of the curve, which are given in Table II, are useful, although only approximate data. According to this theory the interphase is of the type illustrated above, but in reality the interphase is no longer completely polarisable, because at potentials so positive as to be within 0.2 volt of the discharging potential of the anion, mercurous ions can cross the phase boundary. Hence the state of the interphase just illustrated would change, by electrolysis and yield XIV. It is uncertain in which of these states the interphase should be considered to exist, but this uncertainty is not serious because in the absence of a boundary impermeable to charged particles, and in particular, to mercurous ions, the two states are for practical purposes identical.

Metal.	Solution.
+	I -
	Hg <sub>2</sub> I <sub>2</sub>
+	I -

XIV.

The transitional positive branch of the charge-potential curve can also be obtained by starting with a non-polarisable interphase, and then altering the conditions so as to make it more and more polarisable. Thus the extreme positive end of the curve shown in Fig. 4 for a molal solution of nitrate ions was obtained as follows: When mercury is in contact with a normal solution of mercurous nitrate, the interphase is non-polarisable, and the potential difference across it is controlled by the concentration of mercurous ions in the solution. If this potential difference and the interfacial surface tension are measured for this solution, and also for a series of other solutions prepared from it by diluting it with increasing amounts of M/1 potassium nitrate solution (so as to keep the nitrate ion concentration constant) an electrocapillary curve can be plotted. The possibility of working in this way was demonstrated by Nernst as long ago as 1897. Unfortunately the surface tensions cannot be measured in a capillary electrometer because of the tendency of the mercury meniscus to stick to the walls of the capillary in these solutions, and for this reason the drop-weight method for measuring the surface tension has to be used. This method involves special difficulties concerning the control and measurement of the potential of the dropping mercury, and failure in the past to recognise these has resulted in claims being made that electrocapillary

maxima exist in this positive region of potential as well as in the normal place.<sup>28</sup> The present work, as illustrated by the curve in Fig. 4, agrees with that of Frumkin and Obrutschewa<sup>29</sup> in that no such maxima can be detected.

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<sup>28</sup> K. Bennewitz and A. Delijannis, *Z. physikal. Chem., A*, 1927, 125, 144;  
K. Bennewitz and K. Küchler, *ibid.*, A, 1931, 153, 443.

<sup>29</sup> A. Frumkin and A. Obrutschewa, *ibid.*, 1928, 138, 245.

## IONIC CONCENTRATIONS AT INTERFACES.

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The  $\zeta$ -potential of the colloid chemist can be identified with the potential in the neighbourhood of a simple ion at the distance of closest approach of another, as considered in the Debye-Hückel theory. We are familiar with the latter potential determining the average concentration of other ions at the distance considered. The influence of this ionic redistribution on observable properties is usually evaluated through its influence on the potential causing it. It is legitimate, and in some cases simpler, to consider the influence of this redistribution directly. This line of argument is of especial value when we are dealing with the large multivalent ions of colloidal solutes, and the method throws some useful light on several phenomena. Nevertheless, the fact, that the  $\zeta$ -potential determines the local ionic concentrations near the surface of the particle, seems generally to have been overlooked by experimental workers.

We will first consider the local concentration method as applied to equilibria in simple electrolytes. Let the hydrogen ion and the anion  $\text{Ac}^-$  of a weak electrolyte be unable to approach within a distance  $a$  between centres without formation of a covalent molecule of the acid  $\text{HAc}$ . The potential due to each ion at the distance of closest approach of the other will then be  $\frac{\epsilon}{D} \cdot \frac{1}{a}$  if the solution is infinitely dilute, and, according to the first approximation of the Debye-Hückel theory, it will be  $\frac{\epsilon}{D} \left[ \frac{1}{a} - \frac{\kappa}{1 + \kappa \cdot a} \right]$  at finite ionic concentration,  $\kappa$  being the characteristic reciprocal length of the theory (inverse thickness of the ionic atmosphere). The theory is concerned with the effect of this extra term on various equilibrium properties, and by consideration of the work of discharging the ions at finite concentration and recharging them at infinite dilution the value of the mean activity coefficient  $f$  can be calculated, giving

$$-\log_e f = \frac{1}{2} \frac{\epsilon^2}{DkT} \cdot \frac{\kappa}{1 + \kappa a} \quad \dots \quad (1)$$



Applied to the equilibrium between undissociated and dissociated acid, this gives

$$K \cdot C_{\text{HAc}} = C_{\text{Ac}^-} \cdot C_{\text{H}^+} f^2 = C_{\text{Ac}^-} \cdot C_{\text{H}^+} e^{-\frac{e^2}{DkT} \frac{\kappa}{1+\kappa a}} \quad (2)$$

Now this equilibrium can be considered in another way. We may write

$$K' \cdot C_{\text{HAc}} = C_{\text{Ac}^-} \cdot (C_{\text{H}^+})_a \quad (3)$$

where  $(C_{\text{H}^+})_a$  is the concentration (averaged over a sufficient time) of hydrogen ions at the distance of closest approach about each acid anion, *i.e.*, the concentration of hydrogen ions in a position where the formation of covalent acid is possible. By the Boltzmann expression

$$(C_{\text{H}^+})_a = C_{\text{H}^+} \cdot e^{\frac{e^2}{DkT} \left[ \frac{1}{a} - \frac{\kappa}{1+\kappa a} \right]} \quad (4)$$

$C_{\text{H}^+}$  being the average bulk hydrogen ion concentration as before. By combining (3) and (4) we obtain

$$K' \cdot e^{-\frac{e^2}{DkT} \cdot \frac{1}{a}} \cdot C_{\text{HAc}} = C_{\text{Ac}^-} \cdot C_{\text{H}^+} e^{-\frac{e^2}{DkT} \cdot \frac{\kappa}{1+\kappa a}} \quad (5)$$

Since this equation must approach the form of the law of mass-action at infinite dilution ( $\kappa = 0$ ), we may identify  $K' e^{-\frac{e^2}{DkT} \cdot \frac{1}{a}}$  with the ordinary dissociation constant  $K$ . We see then that equations (2) and (5) are identical.

Similar identity of result can be shown in more complex cases, for ions of different valence, etc., and the necessity of the agreement can be shown by more general methods. We may work *either* with *bulk concentrations and activity coefficients* or with *local concentrations* of one kind of ion (in the regions where it may react with the other) and *without activity coefficients*.

The exponential factor on the left side of equation (5) represents an electrostatic factor, which is included in the dissociation constant as ordinarily measured. This factor is of experimental significance in the Wien effect (increase of conductivity in very strong fields) in weak electrolytes. The ionic atmosphere has a twofold influence on the conductivity of weak electrolytes. Owing to its existence, each ion finds itself in a higher local concentration of the other than would be the case were there no atmosphere, and, owing to the localisation of opposite charge in the atmosphere, the central ion is partly screened from the external field. Only the second effect is normally considered in electrolyte theory. It increases with increase of concentration, and is removed when the ions migrate too rapidly for the atmosphere distribution to be reformed. The second effect persists into very dilute solutions and effects the degree of dissociation, if this is not complete. Removal of the atmosphere in very strong fields will bring the ions into an environment of the opposite ions at the average bulk concentration. Dissociation will therefore increase. The electrostatic factor will be removed, and the acid will behave as if it had the dissociation constant  $K'$  above instead of  $K$ . It is not practicable to use fields strong enough to carry this increase of dissociation to its saturation value, but the existence of a very large Wien effect in weak electrolytes is easily explained in this way. The early idea of "Stossionisation," implying an

actual tearing apart of the ionisable molecule, is thus seen to be unnecessary, and a simple calculation will show that such a disruption is impossible, the energy available being far too small. This very simple explanation of the "abnormal" Wien effect in weak electrolytes is somewhat hidden in the elaborate mathematical treatment of Onsager.<sup>1</sup>

An electrostatic contribution to a limiting (infinite dilution) dissociation constant is considered in Bjerrum's treatment<sup>2</sup> of the dissociation constants of dibasic acids. If two carboxyl groups are in equivalent positions in a molecule and sufficiently far separated from one another by a saturated chain for there to be no internal "chemical" effect of one on the other, the second dissociation constant will not be exactly one-half that of a chemically equivalent solitary carboxyl group, as expected on a simple statistical theory, but will be smaller by a factor due to the effect of one ionised group in increasing the local hydrogen ion concentration about the other. This factor will be  $e^{-\frac{e^2}{DkT} \cdot \frac{1}{b}}$  where  $b$  is the distance between the centres of the ionized carboxyl groups. Combining this with the electrostatic factor for the ionized group under consideration, we have, for the second dissociation constant (at infinite dilution)

$$K_2 = \frac{1}{2}K' \cdot e^{-\frac{e^2}{DkT} \cdot \frac{1}{a}} \cdot e^{-\frac{e^2}{DkT} \cdot \frac{1}{b}} \quad (6)$$

We may examine this effect experimentally by removing one ionic group. The second exponential factor and the statistical factor are eliminated. The first exponential factor does not differ in kind from the second. Since, however, it can only be eliminated (and that not completely) by making conductivity measurements in very strong fields, it is convenient to include it in the empirical dissociation constant for the group concerned.

Let us now suppose that this same acidic group is situated on the surface of a large and highly charged colloidal particle, the potential near the surface of which is greater than the average for the whole solution by an amount  $\zeta$ . The hydrogen ion concentration near the surface will be  $e^{-\frac{e\zeta}{kT}}$  times the hydrogen ion concentration in bulk. The effective dissociation "constant" will therefore be

$$K_s = K \cdot e^{-\frac{e\zeta}{kT}} \quad (7)$$

The quantity  $kT/e$  is the familiar  $RT/F$  of galvanic cell theory, and we may therefore conveniently remember that it has the value 60 millivolts at 25° C., when multiplied by  $\log_{10} e$  to convert to the decadic system. (7) thus becomes (at 25° C.)

$$(P_K)_s = P_K - \zeta/60 \quad (8)$$

$p_K$  being  $-\log_{10} K$  and  $\zeta$  being measured in millivolts. Since  $\zeta$ s of the order of 100 millivolts and more are not infrequent, it is evident that apparent dissociation constants in colloidal systems can be very greatly altered.

<sup>1</sup> Onsager, *J. Chem. Physics*, 1934, **2**, 599.

<sup>2</sup> Bjerrum, *Z. physik. Chem.*, 1923, **106**, 219.

Alternatively we may write

$$(\rho_H)_s = (\rho_H)_b + \zeta/60 \quad . \quad . \quad . \quad . \quad (9)$$

where  $s$  and  $b$  denote surface and bulk quantities, and then employ the ordinary dissociation constant in considering equilibria at the surface.

Application of the Debye-Hückel theory in any form to equilibria in colloidal systems is greatly complicated by the fact, that a large fraction of the atmosphere effect about a colloidal ion arises in the region where  $\epsilon\psi/kT$  is not only not much less than one, contrary to the assumption of the simple theory, but is in most cases considerably greater than one. This is not due to  $\psi$  attaining greater values near colloidal ions than near simple ones, but is due to the volume in which it is greater than the theory allows being much larger (even relative to the charge) in the case of the colloidal ion.

This fact carries with it an equally important corollary. In consequence of the much smaller curvature of the surface of the colloidal particle, both the field-strength, and, especially, the divergence of the field, near the colloidal particle, will be much less than near a simple ion whose surface is at the same potential. (The fact that the potential of the surface is not microscopically uniform is here neglected.) Consequently, the orientation of the solvent dipoles, which is governed by the field-strength, and, in particular, the hydration of the particle (attraction of oriented dipoles), which depends upon the divergence of the field, will be less for a colloidal particle than for a simple ion. Thus equation (7) (for a colloidal ion) will be much less invalidated by the dielectric saturation and by hydration than will the exponential correction in the left-hand side of equation (5) (for a simple ion). It has been shown<sup>3</sup> that, in the dibasic acid case (equation (6)), the second exponential term gives approximately correct results without correction for decrease of dielectric constant when  $b$  is greater than 6 Å. The extra effect on an ion situated on a colloidal particle due to the presence of the other ions would be expected to involve less dielectric disturbance than in this case. Thus for 20 charges situated on the surface of a sphere of 27 Å radius, the field at the surface will be about equal to the field at a distance of 6 Å from a single charge; the divergence of the field will therefore only be about 2/9th as great.

We are thus, in applying Debye-Hückel methods to colloidal electrolytes, on safer ground as regards physical assumptions than in dealing with high-valent simple electrolytes. The difficulty is in calculating the effect of concentration on potential. As against this difficulty we can set the advantage of being able to measure  $\zeta$  with more exactness by means of electro-kinetic measurements. If we are dealing with particles so large that the " $4\pi$ " formula of Helmholtz is applicable, we put

$$u = \frac{\zeta D}{4\pi\eta} \quad . \quad . \quad . \quad . \quad (10)$$

where  $u$  is the velocity of the particle in unit field. Substituting in the general counterpart of equation (9) we find

$$(\rho_H)_s = (\rho_H)_b + \frac{4\pi\eta}{D} \cdot \frac{\epsilon}{kT} \cdot \log_{10} e \cdot u = (\rho_H)_b + A \cdot u \quad . \quad (11)$$

<sup>3</sup> Ingold and Mohrhenn, *J.C.S.*, 1935, 949.

$u$  being here reckoned negative for motion towards the anode, positive for motion towards the cathode. For small particles the factor 4 will be replaced by 6. At 25° C. in water  $A$  will have the values 0.325 and 0.217 for small and large particles respectively, if  $u$  is measured in  $\mu$ /sec. per volt/cm., and 0.0340 and 0.0226 if  $u$  is measured in ordinary mobility units ( $\text{ohm}^{-1}$  litres (gm. equiv.) $^{-1}$ ).

The extremely simple relationship expressed in equation (II) (and analogous relationships for ions other than  $\text{H}^+$ ) will give, we believe, a better approximation in dealing with equilibria on the surface of colloidal particles than much more complicated extrapolations of activity coefficient formulæ.

As an example of the way in which this equation might be useful, we may consider the electrometric titration of proteins. If mobility measurements were made on the same systems as arise in the titration, we should use equation (II) to correct the observed  $p_{\text{H}}$  values to give the  $p_{\text{H}}$  at the surface of the particles. The plot of  $(p_{\text{H}})_s$  against amount of acid and base added could then be analysed directly to give more reliable information than would otherwise be obtained about the amino-acid constitution of the protein.

Other applications of this equation which we should like to mention are :—

(1) Interfacial tension- $p_{\text{H}}$  curves for systems containing fatty acids or other amphipathic weak electrolytes. A marked fall in tension is not observed until the  $p_{\text{H}}$  has been increased to a value considerably above  $p_{\text{K}}$  for the acid in question.<sup>4</sup> Danielli<sup>5</sup> has appreciated that the difference between  $(p_{\text{H}})_s$  and  $(p_{\text{H}})_b$  is responsible for this effect, but was not able to make a quantitative estimate of the displacement, owing to there being no simple relationship between the extent of ionisation of the adsorbed layer and the interfacial tension. Cataphoresis measurements on oil droplets in the same system, coupled with the application of equation (II) would take the understanding of this subject considerably further.

(2) The rate of accommodation of surface and interfacial tension to its equilibrium value in solutions of paraffin-chain salts has been found to be very slow in dilute solutions.<sup>6</sup> Doss<sup>7</sup> has recently proposed an electrical potential barrier in the diffuse double layer as the explanation of this effect. Diffusion of the paraffin-chain ions into the interface takes place in effect, not from the bulk concentration  $\bar{c}$ , but from the

local concentration  $\bar{c} \cdot e^{-\frac{e\psi_0}{kT}}$ . This author has not apparently appreciated that  $\psi_0$  can be identified with the  $\zeta$  potential which could be obtained from cataphoretic measurements. Since the mobility of paraffin-chain salt micelles appears to be never much greater than 60 at 25° C., we should not anticipate a retardation of equilibrium from this source of more than about one hundred-fold. Actually, according to the calculations of Doss, retardation may be ten or more times greater than this. It must be pointed out, however, that cataphoresis measurements at the relevant dilutions do not yet appear to have been made,

<sup>4</sup> Peters *et al.*, *Proc. Roy. Soc. A*, 1931, **133**, 140; *Trans. Faraday Soc.*, 1938, **34**, 1537.

<sup>5</sup> Danielli, *Proc. Roy. Soc. B*, 1937, **122**, 155.

<sup>6</sup> Adam and Shute, *Trans. Faraday Soc.*, 1938, **34**, 758.

<sup>7</sup> Doss, *Koll Z.*, 1939, **86**, 205.

and it is possible that they will show a velocity in excess of that shown by the micelle itself at necessarily higher concentrations.

(3) Reaction velocity at interfaces. The efficacy of the Twitchell<sup>8</sup> process for the acid hydrolysis of fats, in which the molten fat is emulsified by a paraffin-chain salt with a strong acid head group, may be compared with the relative lack of advantage in emulsifying an ester in alkaline hydrolysis.<sup>9</sup> The emulsion particle being in all cases examined negatively charged, the surface acid concentration is greater than that in the bulk; acid hydrolysis is therefore favoured by the charge, and alkaline hydrolysis is depressed.

We do not suggest that the displacement of  $p_H$  is capable alone of explaining all the observations we have briefly mentioned. It is, however, an important factor, the magnitude of which could be estimated from readily obtainable experimental data in the majority of cases. If the appropriate correction, certainly correct as regards order of magnitude, were thus made, we should be in a better position to estimate the significance of other factors, such as a real change in the dissociation constant of an acid, due to the unionised acid being really dissolved in an oil rather than in a water phase, or due to reacting ions or molecules being obstructed by adsorbed non-reactive molecules, etc.

From a consideration of the effect of the  $\zeta$ -potential in determining ionic concentrations at interfaces, it is an obvious step to inquire whether we can use measurements of ionic equilibria at interfaces to estimate this potential.

We require for this purpose measurements of the acid-base equilibrium of a substance present in a system entirely, or almost entirely adsorbed at an interface. It is necessary therefore to make measurements on very small concentrations without disturbing the equilibria concerned. The only possibility seems to be to use indicators which change colour when the equilibrium is shifted.

We have been engaged in experimental work on systems of this type, where our interface is that of the amicroscopic micelles of an aqueous paraffin-chain salt solution. Such systems are very suitable because the liquid micelle has a great ability to incorporate foreign ions and molecules, and because the optical clarity of the solutions permits more accurate measurements than would be possible in a relatively coarse emulsion. Very great displacement of indicator equilibria in strongly buffered solutions on the addition of small amounts of paraffin-chain salts had been previously noticed.<sup>10</sup> Such displacements are most easily interpreted as a migration of the indicator to the micelle surface where the  $\zeta$ -potential causes the  $p_H$  to be considerably different from the value in the bulk of the solution. It is consistent with this explanation that the paraffin-chain cations cause a displacement to the alkaline side, and paraffin-chain anions a displacement to the acid side. Moreover, the maximum displacements usually obtained correspond to  $p_H$  displacements of about 2 units, and according to equation (11) such would be expected for mobilities of the micelle (at 25° C.) of the order of 60 units, which is in fact about the maximum observed.

A suitable indicator for quantitative work must fulfil the following conditions:—

<sup>8</sup> Twitchell, *J. Am. Chem. Soc.*, 1906, 28, 196.

<sup>9</sup> King and Mukherjee, *J. Soc. Chem. Ind.*, 1938, 57, 431.

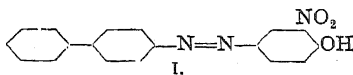
<sup>10</sup> Hartley, *Trans. Faraday Soc.*, 1934, 30, 444.

(1) It must be found almost exclusively in the micelle rather than in the water, even under the least favourable conditions.

(2) The ionizable group must be situated in the interface rather than in the interior of the micelle.

(3) The optical density of each form of the indicator, by itself, should not be influenced by the concentration of paraffin-chain salt.

In any particular case an indicator showing colour change in the suitable  $p_H$  range must be chosen. Diphenylazo-*o*-nitrophenol (I) was chosen for the present work. That it fulfils the conditions set out above was shown by the following observations :



(1) Partition experiments showed that even in the ionised (alkaline) form this indicator is found almost entirely in the micelles in a dilute cetane sulphonate solution. (2) The solubility of the acid form in an acid cetane sulphonate solution was much greater than would be the case were the indicator acid dissolved only by the paraffin interiors of the micelles. (3) In neither form does this indicator carry a charge of opposite sign to the paraffin-chain ions used in this work, and therefore any possible change in the nature of the interface will not be likely to affect the electronic structure of the indicator ion or molecule. It was also found experimentally that the colour in neither form varied with the paraffin-chain salt concentration.

The work was actually undertaken in order to determine the concentration of cations at the surface of the micelle in a solution containing almost exclusively a simple paraffin-chain salt, this information being required for a different purpose from that discussed above. It is somewhat less suitable for determining the ratio of cation concentration at the interface to that in bulk owing to the uncertainty about the value of the latter. For this purpose measurements in systems containing an excess of simple electrolyte would be preferable.

Triethanolammonium cetane sulphonate was used as the paraffin-chain salt and the very low bulk hydrogen ion concentration was controlled by the addition of free triethanolamine to the system. Pure triethanolamine was used. The  $p_K$  for triethanolamine was taken to be 7.80 as found for 25° C. by Sprinkle and Hall.<sup>11</sup> Determination of  $p_K$  for the indicator was a matter of some difficulty on account of the extremely low solubility of the acid form. A very long column of solution in triethanolamine-triethanolammonium chloride buffers was used, and fairly consistent values of 6.35 obtained. Concentrations of indicator ion and molecule were measured by means of light-absorption using a photoelectric photometer calibrated by standard solutions. Details of these experiments will be published elsewhere. Similar measurements with higher concentrations of indicator were made in triethanolammonium cetane sulphonate-triethanolamine buffers. From these experiments ( $p_H$ )<sub>0</sub> could be directly calculated. In order that measurements could be made in the most sensitive  $p_H$  region, two different ratios of the concentrations of the buffer constituents were used, the one giving better results at lower ionic concentrations and the other at higher. Since there is no appreciable change in ionic concentration when the concentration of the base alone is changed, it can be assumed that the hydrogen ion concentration in a solution of given salt concen-

<sup>11</sup> Hall and Sprinkle, *J. Am. Chem. Soc.*, 1932, 54, 3469.

tration is everywhere inversely proportional to the concentration of base. This could be confirmed where the two curves overlapped.

An attempt to estimate the bulk hydrogen ion concentration was made by similar measurements using a "non-adsorbed" indicator in place of the amphipathic one; *p*-nitrophenol was chosen. Even this, however, is not exclusively found in the aqueous phase. The solubility of acid nitrophenol in water is considerably increased by addition of the paraffin-chain salt. When the concentration of the latter is 0.03 N, the increment of solubility is 58 per cent. Assuming a constant partition ratio for the acid between micelle and water the observed  $(pH)_b$  was corrected for this effect. The  $pK$  of nitrophenol was determined in triethanolamine-triethanolammonium chloride buffers.

In Fig. 1 the value of  $(pH)_s$  (upper curve) and  $(pH)_b$  are shown plotted against the square root of the concentration of triethanolammonium cetane sulphonate. The points on this graph are calculated from the experimental data to represent  $(pH)_s$  and  $(pH)_b$  in solutions containing equivalent quantities of salt and free base. The "ideal"  $pH$  of such

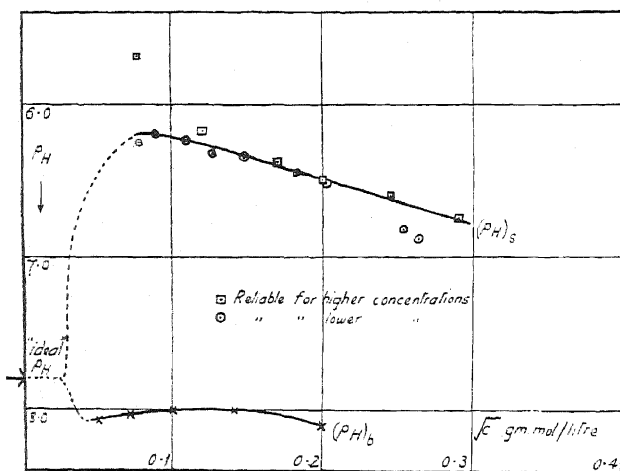


FIG. 1.

a solution is shown by the arrow in Fig. 1. All the indicator measurements were made at 30° C.

There are two sources of uncertainty in the values of  $(pH)_b$  shown in Fig. 1: firstly, the partition ratio of *p*-nitrophenol between water and micelle has been determined for only one concentration of paraffin-chain salt; secondly, and more important, because the solubility of *p*-nitrophenol is relatively high, it has only been possible to determine the partition ratio at a concentration of nitrophenol some hundred times greater than that at which it was employed as an indicator. Since in such a concentrated solution of nitrophenol the constitution of the micelle is radically altered, it is not to be expected that the partition ratio which has been determined will apply to more dilute solutions. So long as the second uncertainty remains, the first is of little importance.

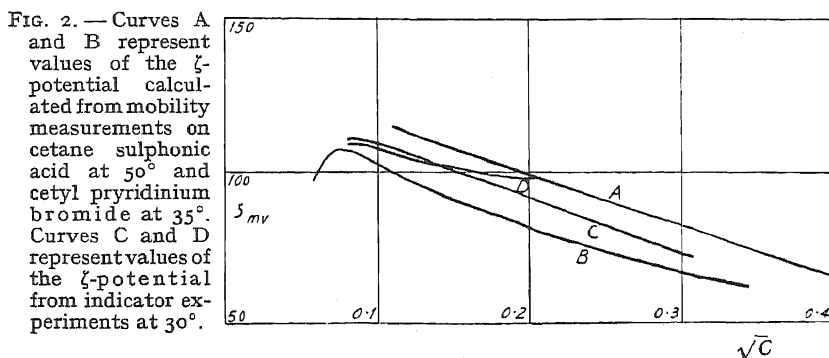
At 30° C. equation (9) becomes

$$(pH)_s = (pH)_b + \zeta/61.$$

Using this equation,  $\zeta$  has been calculated from the observed values of  $(pH)_s$  on the assumption that  $(pH)_b$  has the value 8.0 independently of

paraffin-chain salt concentration. These values of  $\zeta$  give curve C in Fig. 2. Curve D shows the values of  $\zeta$  obtained by using the values of  $(p_H)_b$  shown in Fig. 1.

Curves A and B represent  $\zeta$  calculated by means of the "6 $\pi$ " formula from the mobility data of Hartley and Samis<sup>12</sup> for cetane sulphonate in cetane sulphonic acid and for cetyl pyridinium in cetyl pyridinium bromide at 50° C. and 35° C. respectively. Approximately, it is found that the  $\zeta$ -potentials of various paraffin-chain salt micelles under the same physical conditions, as calculated from mobility data, depend upon the chain length and the nature of the head group of the paraffin-chain ion and upon the valence of the gegenion, but not to any marked extent upon the specific properties of the gegenion.<sup>12</sup> Thus we might expect that there will be agreement as regards order of magnitude between the  $\zeta$ -potentials of the cetane sulphonate micelle, which we have



determined by indicator measurements, and the potentials of the micelle of another cetane sulphonate derived from mobility measurements. The expected agreement is exhibited in Fig. 2.

In order to make a critical comparison, it will be necessary to make indicator measurements on solutions, which contain, in addition to the paraffin-chain salt and the free base, a simple salt of the base. This will fix the value of  $(p_H)_b$  and permit a comparison between the  $\zeta$ -potentials so determined and those from mobility measurements on the same systems, from which something might be learnt of the influence of the finite time of relaxation of the ionic atmosphere on the mobility of the micelle.

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<sup>12</sup> Hartley and Samis, *Trans. Faraday Soc.*, 1938, 34, 1288.



## PART II.—THEORETICAL TREATMENT OF THE DOUBLE LAYER AND ITS IMPLICATIONS.

### INTRODUCTORY PAPER.

BY H. R. KRUYT AND J. TH. G. OVERBEEK.

*Received 26th August, 1939.*

As this second part of our Discussion includes (a) the theoretical treatment of the electric double layer; (b) electrokinetics; and (c) their bearing for the stability of colloids, it seems to be useful to consider why these problems are central problems in present day colloid chemistry.

Any material, colloiddally dispersed, is characterised by the facts that it does not tend to molecular dispersity (true solubility) and at the other hand that it is inhibited from forming a coherent phase. Though the possibility has been discussed, whether the cohesion energy would be negative in colloidal systems, it is taken for granted that such is not the case, at least with hydrophobic colloids, but that, in addition to the tendency to cohesion, there exists in these systems a repulsive factor which counterbalances the cohesion tendency.

It was William Hardy who, in 1900, pointed out that there is a relation between electrophoretic mobility and colloidal stability. It is now generally accepted that an electric repulsion inhibits coalescence of the particles in what is called a stable colloidal solution. Though other repulsive factors may interfere also in colloidal solutions, we shall now consider only this electric repulsion.

As mentioned, Hardy had called the attention of colloid-chemist to the close relation between an *electrokinetic* phenomenon and stability; since then, electrokinetics have become a main chapter of colloid-chemistry. Consequently the subject has been treated mostly for the special purpose of explaining colloidal phenomena, and theories have been given, which often accounted in sufficiently for results obtained in other fields of electrochemistry. It will not be necessary to give an account of many errors made in this domain; I want to confine myself only to the remark, that it is psychologically understandable that in the beginning colloid chemistry went its own way with regard to electrokinetics. Helmholtz had given already in 1879 a profound discussion of the electrokinetic phenomena; Gouy in 1910, von Smoluchowski in 1914, and Stern in 1924, on the sound basis of the electric double layer of the Helmholtz paper, developed the theory further. Later, many authors tried to reconcile the data of colloid-chemistry with those of general electrochemistry, and this meeting is a manifestation of that desire.

Now what is the general trend of our now prevailing point of view? We think it can be put in this way:

An electric double layer arises at the boundary of two phases as soon as an ion is distributed unequally in these two phases. When one of the



that neutral (*i.e.* potential non-determining) electrolytes in small concentration caused the  $\zeta$  value calculated according to Helmholtz to increase. As  $\kappa$  the specific conductivity of the electrolyte solution was taken. Now Gortner and his pupils have pointed out that surface conductance played an important rôle with streaming potentials, and a short time ago Rutgers (Ghent), by an ingenious method, took this surface conductance into account and showed that an increase of  $\zeta$  by neutral electrolytes did not exist.

However, this question of high conductivity at the surface is only a detail from a much more important difference between the Helmholtz theory and our modern conception of the double layer.

It has been shown by Bikermann, Henry, Hermans and others, that the electrophoresis equation needs corrections in many respects. In Helmholtz's equation surface conductance was not taken into account, nor was the difference in conductance between the colloidal particle and the surrounding liquid.

Hermans evaluated the influence of the relaxation terms in the complete electrophoresis equations, and found them surprisingly high. In some cases the correction terms for the relaxation effect were even

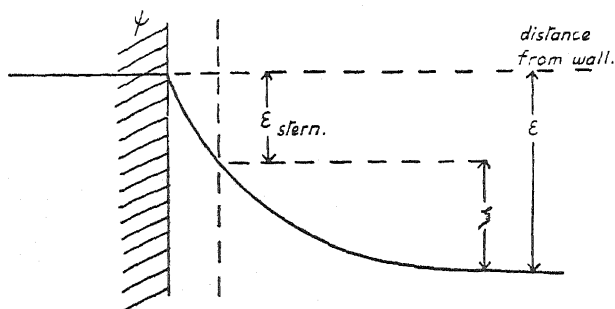


FIG. I.

larger than the main term itself. The evaluation of all these corrections entails very large mathematical difficulties.

So that we do not as yet possess an electrophoresis equation which takes all factors into account.

Owing to these difficulties, one was never certain whether the values calculated for  $\zeta$  were right or not; many authors preferred, therefore, to use the electrophoretic  $u$ -values as a relative measure for  $\zeta$ . Happily last year Dr. H. de Bruyn found a method to determine  $\zeta$ -values not from electrokinetic phenomena, but from mere potential measurements.<sup>1</sup> As his work has not yet been published, we think it desirable to give a short survey of his method and results.

The course of the potential in the double layer may be represented schematically by Fig. I.

Next to the wall (solid phase) there is a steep potential difference  $\epsilon_{\text{Stern}}$  determined by the total charge and by the capacity ( $c$ ) of the Stern layer.

$$\epsilon_{\text{Stern}} = \frac{\text{total charge}}{c_{\text{Stern}}}$$

<sup>1</sup> Recently we found that Levina and Sarvisty (*Acta Physicochim.*, 1937, 7, 485, have also made an estimation of  $\zeta$  by measurements of one voltage.

The course of the potential in the diffuse part of the double layer is determined by Gouy's theory. The potential difference in this Gouy layer will be called  $\xi$ . This may be equal to, or a little bit larger than  $\zeta$  according to where we locate the first layer of liquid which may be sheared along the wall.

Now Dr. de Bruyn's method for measuring  $\xi$  is based upon equation (1).

$$\epsilon = E_0 + \frac{RT}{Z_i F} \ln a_i. \quad (1)$$

The absolute value of the "total potential difference,"  $\epsilon$ , may be found by determining the activity of the potential determining ions in the liquid phase provided  $E_0$  or the value of the zero-point of charge is known.

When a neutral electrolyte is added to the liquid phase, in the first instance the Gouy-layer will become less diffuse, the potential difference  $\xi$  will diminish. The total potential  $\epsilon$  will decrease with the same amount, so that equation (1) is no longer satisfied. This process is represented in Fig. 2 by the arrow 1.

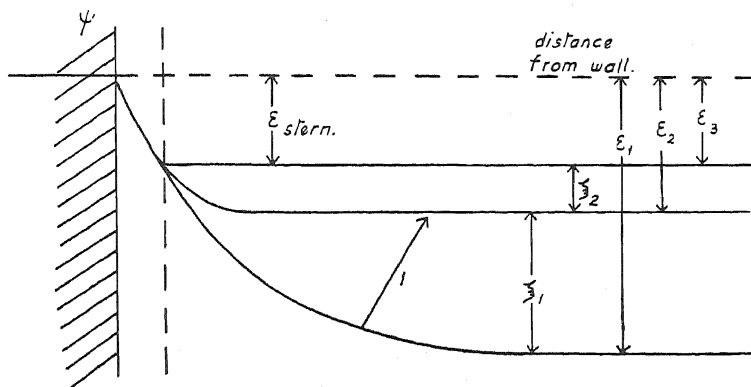


FIG. 2.

Now the wall of the solid phase will take up a number of potential determining ions. This causes  $\epsilon$  to become larger and  $a_i$  to become smaller; until a new equilibrium is reached in which equation (1) is satisfied. *The experimental conditions may be chosen in such a way (small  $a_i$ , large adsorption capacity of the solid phase) that while  $a_i$  does diminish,  $\epsilon$  does not increase measurably.* In that case the value of  $a_i$ , after the new equilibrium establishes itself, determines immediately the value of  $\epsilon_2$ , and the difference  $\epsilon_1 - \epsilon_2$  just equals the amount  $\xi_1 - \xi_2$  with which the potential in the diffuse part of the double layer has diminished. If the quantity of added salt has been great enough to suppress the diffuse double layer completely, the value of the potential  $\xi_1$  of the Gouy layer may be set equal to the difference  $\epsilon_1 - \epsilon_3$ .

The value of  $\epsilon_1 - \epsilon_2$  is given by

$$\epsilon_1 - \epsilon_2 = \frac{RT}{Z_i F} \ln \frac{a_{i_1}}{a_{i_2}}. \quad (2)$$

The activity of the  $i$ -ions may be determined by measuring the potential difference  $P$  between a reference electrode and an electrode which is reversible on the  $i$ -ion.

Than

$$P_1 = P_N + \frac{RT}{Z_i F} \ln a_{i_1}$$

$$P_2 = P_N + \frac{RT}{Z_i F} \ln a_{i_2}$$

From which follows

$$\frac{RT}{Z_i F} \ln \frac{a_{i_1}}{a_{i_2}} = P_1 - P_2 \quad (3)$$

Combining equations (2) and (3) one finds

$$\xi_1 - \xi_2 = \epsilon_1 - \epsilon_2 = P_1 - P_2 \quad (4)$$

*The change of the potential difference in the diffuse layer is equal to the directly measurable change of the potential of the  $i$ -electrode.*

To demonstrate the usefulness of this new method we will quote some examples from the work of Dr. de Bruyn.

We start with a fine suspension of AgI in a liquid in which the activity of the  $I'$  ions equals  $a_v = 10^{-10}$ . At this  $a_v$  the AgI is uncharged;  $\epsilon$  and  $\xi$  are both equal to zero.

The potential difference between an AgI-electrode and a reference electrode (e.g., a glass electrode or a calomel electrode) dipped in this system is measured and called  $P_0$ . A small quantity of a NaI solution is added now to the suspension and, after establishment of the adsorption equilibrium, the new potential difference  $P$  (and therewith the activity of the  $I'$ -ions) is determined.

The difference between  $P$  and  $P_0$  is equal to the "total potential difference" after addition of the NaI.

The concentration of the suspension is chosen so large that the free  $I'$ -ions form only a very small fraction of the total quantity of  $I'$ -ions that has been added and we may identify the adsorbed  $I'$  ions to the added quantity of  $I'$ -ions. In this way the total potential difference  $\epsilon$  may be determined as a function of the

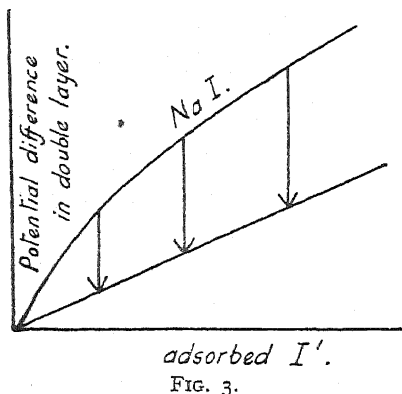


FIG. 3.

amount of adsorbed  $I'$ -ions, that is of the charge of the suspension.

The curve marked NaI in Fig. 3 illustrates this relation

If neutral electrolytes are added to such a suspension, which has been charged by NaI, the accompanying changes in the diffuse double layer manifest themselves in the change of potential of the AgI electrode.

Fig. 4 shows the changes of double layer potential brought about by different electrolytes in a suspension of AgI which had been charged previously by NaI to a total potential difference of 230 mV.

Attention is called to the influence of the valency of the counter-ions but also to the fact that the final decrease of potential is independent of the valency-type, provided the quantity of added salt is large enough to suppress the diffuse double layer. The potential is not decreased until zero but the lowest value reached (130 mV in this case) represents the remaining potential difference of the Stern layer.

The difference  $230 - 130 = 100$  mV represents the  $\xi$  potential of the suspension before addition of the neutral salts. This value is somewhat

larger than the  $\zeta$ -values found by electrophoresis measurements, but the difference may be probably fully accounted for by the imperfections of the electrophoresis-equation.

The influence of neutral electrolytes has been investigated in various states of charge of the suspension, so determining which part of the total potential difference belongs to the Gouy-layer and which part to the Stern-layer. In Fig. 3 this has been represented by arrows departing from different points of the NaI curve. The heads of the arrows may be connected by a curve, which must represent the potential difference of the Stern-layer as a function of the amount of adsorbed  $I'$  ions.

It is a strong support to the theory here developed, that this curve comes out to be a straight line, in full accord with the capacity of the Stern-layer (*i.e.*, total charge/ $e_{\text{Stern}}$ ) being a constant.

Although, in many cases, colloid chemistry is more interested in the potential of the double layer than in its charge, a full knowledge of the structure of the double layer requires a knowledge of the charge as well. The theory of Stern, which we may say is generally accepted nowadays,

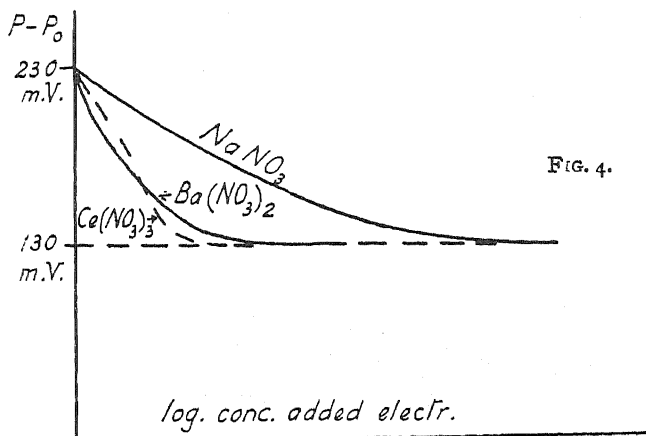


FIG. 4.

owes its existence to the fact that neither Helmholtz' nor Gouy's theory could account for the capacity of the double layer on mercury.

Determination of the charge of a double layer from electrokinetic phenomena is impracticable owing to the great mathematical difficulties. Moreover the charge determined in this way would only represent the charge of the mobile part of the double layer and would be smaller (in most cases much smaller) than the total charge.

Apart from that, determination of the charge generally presents less difficulties than the determination of the potential. The difficulties here are of a more experimental character, owing to the smallness of the charge.

The first values for the charge of the double layer have been obtained in the case of a mercury surface, during researches on the electrocapillary curve.

With colloids most determinations of the charge are based on chemical determinations of the bearers of the charge (*i.e.*, the ions). The most simple and convenient method is the titration of the counter-ions. Pauli was the first to show, that a great many negative sols may be dialysed so sharply, as to expel practically all foreign electrolytes and

replace all the counter-ions by H-ions. By direct conductometric or potentiometric titration of such a sol with NaOH the total charge may be determined with accuracy.

In other cases it is possible to determine directly the quantity of peptising ions (*e.g.*, in the AgI sol the peptising  $I'$  ions may be titrated with  $AgNO_3$ ). The determination of the maximum exchange capacity of the double layer may be mentioned as a third method.

In the case of the AgI sol these three methods have been used independently and have given results, that are completely concordant among each other. We may infer herefrom that the determination of the total charge of colloids rests on a very sound base.

In drawing theoretical conclusions from this total charge there arises, however, a very serious difficulty. It is not enough to know the total charge in a certain portion of a sol; one has also to know the charge of a single particle or the charge per  $cm.^2$  of surface; and it is well known that determination of the dimensions of colloidal particles has always been affected by very large experimental errors.

So far the present considerations on the *capacity* and the *charge* of the double layer in colloids are attended with great uncertainty. In this field of research the mercury surface remains the ideal object.

On the other hand, we have available, for the measurement of *potentials* in the double layer, various methods, applicable to micro as well as to macro phase-boundaries, the results of which have been roughly concordant. It will be one of the tasks of the near future to compare these different methods in a more exact and systematic way.

From what we have said above, it will be obvious that our knowledge of the mechanism of the double layer is still very incomplete. It is evident that the problem of colloid stability, as determined by the electric protection of the double layer is still more complicated and uncertain. We do not doubt that Hardy's fundamental conception is in principle, right, but the numerous investigations of Burton, Powis, Freundlich, Limburg, Briggs and many others, indicate that a simple relation between electrophoretic mobility and colloid stability does not exist. This is clear if  $\zeta$  governs stability; for we have seen that the proportionality between  $\zeta$  and  $u$  is mostly dubious. However, severe doubt has arisen whether  $\zeta$  is a direct measure for stability. Eilers and Korff have pointed out from dimensional considerations, that  $\zeta$  could not be the repulsive energy, that only  $\zeta^2$  multiplied by a length could play such a rôle. They assumed from the Debye theory to be that length; several other scientists made other assumptions. At the moment, as we start this Discussion, the question is still unsolved.

## PART II.—(A) ELECTROKINETIC EQUATIONS.

### THE STUDY OF THE DOUBLE LAYER AT THE METAL-SOLUTION INTERFACE BY ELECTROKINETIC AND ELECTROCHEMICAL METHODS.

By A. FRUMKIN.

*Received 18th July, 1939.*

#### 1. Elektrokinetic Behaviour of Metals.

There exist a number of experimental methods which allow the study of the double layer at the metal-solution interface. They may be classified as follows:

(1) Direct measurement of the surface charge (adsorption measurements, charging of a freshly formed surface), or of its variation with the potential (capacity measurements).

(2) Indirect determination of the surface charge from electrocapillary data.

(3) Measurement of the total potential difference under non-equilibrium conditions (dropping electrode, overvoltage measurements in dilute solutions).

(4) Elektrokinetic measurement.

(5) Contact angle measurement.

As well known, the data obtained by different methods could not be reconciled for a long time; these discrepancies led to a large extent to a discussion as to the position of the zero point of the charge of metals, and the controversy about the relative value of the zero points of Billitzer and Ostwald-Nernst filled the electrochemical literature during many years.<sup>1</sup> One of the possible causes of such discrepancies has been pointed out by Smoluchovski and Freundlich, who have indicated that the electrokinetic behaviour of metals is determined not by the total potential drop between the metal and the solution, but only by that fraction of it which corresponds to the movable part of the surface layer ( $\zeta$  potential). Equally important was probably the circumstance that, often, results of measurements carried out by various methods with different metals were compared, without taking into account that the position of the zero point changes with the nature of the latter. Finally, it is necessary to take into account, when comparing electrokinetic data with the results obtained by other methods, the complications in the structure of the double layer, connected with the formation of oxide and hydride films on the surface of the metal.

<sup>1</sup> Billitzer, *Drüdes Ann.* II, 1903, 902; *Trans. Am. Elektrochem. Soc.*, 1930, 57; Palmer, *Z. physikal. Ch.*, 1907, 59, 129; Frumkin, *Sov. Phys.*, 1933, 4, 239; Freundlich and Mäkelä, *Z. Elektrochem.*, 1909, 15, 161.



The discrepancy between the electrokinetic and electrode behaviour of metals which is observed if all the above-mentioned circumstances are left out of account, is so large that colloid chemists used to distinguish sharply the two groups of phenomena; thus, for instance, in their well-known monograph Pauli and Valkó<sup>2</sup> say: *kann man trotzdem die Nernst'sche Lösungstension für die Ladung der Teilchen verantwortlich machen? Die experimentell festgestellte Unabhängigkeit geht so weit dass wir diese Möglichkeit für äusserst unwahrscheinlich halten müssen.* In reality, however, when electrokinetic and electrochemical measurements are carried out with the same surface and when the behaviour of the system is not complicated by the phenomena of specific adsorption, the determination of the sign of the surface charge by various methods must give coinciding results. This conclusion was confirmed by the investigations of N. Bach and others in this laboratory with activated charcoal, the potential of which was changed gradually from a saturation of its surface with oxygen to a saturation with hydrogen.<sup>3</sup> In this case, the sign of the charge and the position of the zero point of the charge of the activated charcoal determined from electrokinetic and adsorption measurements exactly coincided. On the other hand, it can be shown that adsorption measurements give actually a picture of the origin of the total potential drop on a charcoal electrode, for this potential varies over a very wide range according to a linear law, as a function of the charge as determined from adsorption measurements.<sup>4</sup>

I shall consider in more detail the properties of the platinum electrode. Measurements of the adsorption, carried out with platinised platinum at various potentials,<sup>5</sup> have shown that with a reversible hydrogen potential the platinum surface is negatively charged and adsorbs cations; with the transition to more positive potentials the adsorption of cations, as would be expected, decreases at first and is further replaced by the adsorption of anions. In an acidulated normal solution of  $\text{Na}_2\text{SO}_4$ , where the specific adsorption of the anions can probably be neglected, the zero point of the charge lies at a potential  $\phi = 0.12$  with respect to the normal hydrogen electrode. With further increase of the anode polarisation, the anion adsorption, and consequently the positive surface charge, rises until a certain value is reached (in the solution under consideration about  $\phi = 0.7$ ), the further increase of the potential being accompanied by a decrease of the positive charge, which in not very acid solutions changes its sign once more and becomes negative. This anomalous dependence of the adsorption on the potential (as follows from a comparison

<sup>2</sup> Pauli and Valkó, *Elektrochemie der Kolloide*, p. 346, 1929.

<sup>3</sup> N. Bach, *Koll. Z.*, 1933, 64, 153; Pilojan, Krivorutshko and N. Bach, *ibid.*, 287. The results recently obtained by Bennister and King, *J. Chem. Soc.*, 1938, 991, are in contradiction with these conclusions, because according to these authors charcoal activated at  $850^\circ$  in oxygen has a negative electrokinetic potential, in spite of the fact that it adsorbs anions preferentially to cations. It is necessary, however, to bear in mind that, whereas for the charcoals referred to in the papers quoted from our laboratory, it was shown, by specially precise measurements, that the electric potential has identical values at different points of the charcoal surface (Frumkin, Lewina and Zarubina, *Z. physikal. Chem. A*, 1931, 155, 41), the heating of the charcoal in oxygen produces a very inhomogeneous surface (Bruns, Maximowa and Pos, *Koll. Z.*, 1933, 63, 290), which can hardly serve for the elucidation of the above relations.

<sup>4</sup> Bruns, Burstein, Fedotow and Liwshitz, *Acta Physicochim.* 1938, 8, 47, and especially non-published experiments of Burstein and Kuchinski.

<sup>5</sup> Slygin, Frumkin and Medwedowsky, *Acta Physicochimica*, 1936, 4, 911; Frumkin and Slygin, *ibid.*, 1936, 5, 819; also Verwey and De Boer, *Rec. Trav. Chim. P.B.*, 1936, 55, 675.

of the adsorption curves with the charging curves of platinised electrodes) is determined by the appearance at sufficiently high positive potentials of an oxide film and by the circumstance that the linkage between the metal and the adsorbed oxygen is of a dipole character, the oxygen being the negative end of the dipole. The appearance of such an orientated layer of dipoles must at a given potential lead, as it is easy to see, to a sharp decrease of the anion adsorption.

In alkaline solutions, the region of the cation adsorption on a surface covered with adsorbed hydrogen passes continuously into a region of cation adsorption on the oxidised surface, without the appearance of the intermediate interval, where anions are adsorbed, because at those potentials at which anion adsorption would take place, the surface in alkali solutions is already oxidised (see <sup>5</sup> for greater detail).

The particles of ordinary platinum sols when investigated by electrokinetic methods show a negative charge; as a consequence of the conditions under which they are obtained, the surface of these particles must be oxidised, as was usually assumed by colloid chemists,<sup>6</sup> corresponding to the last portion of the above-described adsorption curve.

It follows from what has been said that there must exist, in addition to such a negative oxygen sol of platinum, a negative hydrogen sol corresponding to the first region of the adsorption curve, and a positive sol of platinum corresponding to its middle part. These considerations were put forward by the author in the discussion on colloid electrolytes in 1935,<sup>7</sup> their correctness has been later confirmed experimentally. N. Bach and Balaschowa actually succeeded in obtaining negative "hydrogen" platinum sols,<sup>8</sup> and, moreover, by careful oxidation of the latter, positive platinum sols also.<sup>9</sup> The observation of sols does not, however, allow a quantitative determination of the position of the point of zero charge. It has recently been possible to fill up this gap using, with some refinements, the classical method of Billitzer, *i.e.*, by observation of the deflection of a platinised platinum wire in an electric field.<sup>10</sup> Since conducting bodies can be used in electrokinetic measurements only if their surface is completely polarised under the experimental conditions, the choice of a platinised surface instead of a smooth one seems at first sight inadequate; in reality, however, working with a non-platinised surface in a large volume of liquid, one cannot, even with the most careful purification of the electrolyte, avoid poisoning the surface, which leads to a complete vitiation in the course of the curve. Fig. 1 shows the results of these experiments: the abscissæ give the potential of the wire with respect to a normal hydrogen electrode, the ordinates—the deflection under the action of the field in arbitrary units. The positive sign of the deflection corresponds to a positive charge of the surface. The concentration of the electrolytes was about  $2 \times 10^{-5}$  N. As is seen from curves I and II, referring to HCl and H<sub>2</sub>SO<sub>4</sub>, the change of electrokinetic potential with the polarisation of the wire corresponds exactly to the adsorption data. In the case of anode polarisation the

<sup>6</sup> Pennycuik, *J. Chem. Soc.*, 1927, 2600; *Koll. Z.*, 1929, 49, 407; 1930, 54, 21; *J. Am. Chem. Soc.*, 1930, 52, 4621; Pauli and Baczewski, *Monatshefte f. Chemie*, 1936, 69, 204; Pauli and Schild, *Koll. Z.*, 1936, 72, 165.

<sup>7</sup> Frumkin, *Trans. Faraday Soc.*, 1935, 31, 69.

<sup>8</sup> N. Bach and Balaschowa, *Acta Physicochimica*, 1935, 3, 79; N. Bach and Rakow, *ibid.*, 1937, 7, 85; Zimin and N. Bach, *ibid.*, 1939, 11.

<sup>9</sup> Balaschowa and N. Bach, *Acta Physicochimica*, 1937, 7, 899; *Nature*, 1936, 137, 617.

<sup>10</sup> Balaschowa and Frumkin, *C. R. Acad. Sc. U.R.S.S.*, 1938, 20, 449.

negative charge decreases, and at  $\phi = 0.15 - 0.18$  becomes positive and, after reaching at a certain potential a maximum value, begins to decrease, becoming again negative. In alkaline solution (curve IV) also in agreement with the adsorption data, there is no change of sign of the charge of the wire. A similar result is obtained in the case of an electrolyte, which had not been subjected to a special purification (curve III). A change of sign of the charge of the platinum surface was also observed by Kruyt and Oosterman<sup>11</sup> in their investigation of the flow potentials in platinum capillaries; this method is, however, connected, apparently, with much larger difficulties than that described here.

It follows from the above data that, under adequately chosen experimental conditions, the results of electrokinetic and of adsorption measurements on platinised platinum are in complete agreement; in particular, both methods yield the same position of the zero point. The origin of the total potential drop on the same electrode can be pictured on the

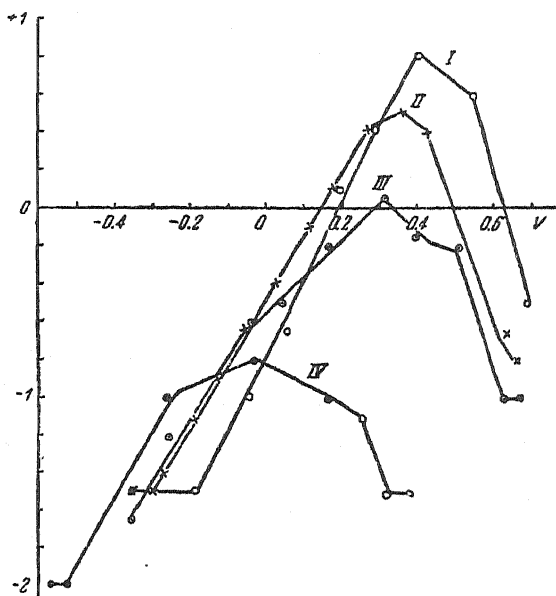


FIG. 1.—Deflection of a platinised platinum wire in an electric field (Balaschowa and Frumkin).

I—HCl, II—H<sub>2</sub>SO<sub>4</sub>,  
III—H<sub>2</sub>SO<sub>4</sub> (without special purification),  
IV—NaOH.

basis of adsorption and polarisation measurements in a way described in detail in the above quoted papers,<sup>5</sup> and also in the paper by Frumkin and Slygin.<sup>12</sup>

The behaviour of a silver electrode will be discussed in a forthcoming publication from this laboratory. Special interest attaches to the comparison of the zero point found by electrokinetic and by other methods in the case of mercury. The researches of a number of authors<sup>13</sup> show that the direction of motion of a drop of mercury in an electric field is actually reversed at a potential which corresponds to the maximum of the electrocapillary curve, i.e. to the zero point of the charge. The observed motions of the mercury drop are produced, however, by surface streamings, connected with a variation of the interfacial tension as a

<sup>11</sup> Kruyt and Oosterman, *Koll. Beih.*, 1938, 48, 377.

<sup>12</sup> Frumkin and Slygin, *Acta Physicochimica*, 1936, 5, 819.

<sup>13</sup> Frumkin, *J. phys. Chem. (russ.)*, 1917, 49, 207; Craxford, *Phil. Mag.* (7), 1933, 16, 268; Craxford, Gatty and McKay, *Phil. Mag.* (7), 1937, 23, 1079.

consequence of the polarisation of the drop, due to the passage of the current; they cannot, therefore, be considered as an electrokinetic phenomenon in the usual sense of this term.<sup>14</sup> This is confirmed in particular by the circumstance that the above agreement is preserved in the presence of capillary active ions, which could not be the case with a true electrokinetic motion. The surface streamings due to a variation of the potential for small polarisations must, on the other hand, always disappear exactly at the maximum of the electrocapillary curve. As has recently been shown, these surface streamings are responsible for the appearance of maxima on current-voltage curves obtained with a dropping mercury electrode.<sup>15</sup>

We will not dwell on the quantitative comparison of the  $\zeta$ -potentials, observed by electrokinetic methods in the case of metallic particles, with the values calculated from the total potential drop with the help of some theory of the double layer. A quantitative theory of electrokinetic phenomena is still beset with too many difficulties in the case of conducting particles; moreover, this question will probably be treated in other communications. It may be possible, however, to determine quantitatively the degree of diffuseness of the double layer on the surface of metals by other methods.

## 2. Electrochemical Methods of Investigating the Structure of the Double Layer.

Starting from the experimentally established fact that the over-voltage  $\eta$  in the discharge of the hydrogen ion on a mercury cathode for a given solution is expressed as a function of the current strength  $i$  by Tafel's relation

$$\eta = \frac{2RT}{F} \ln i + \text{constant},$$

and assuming that only those hydrogen ions are discharged, which come into direct contact with the surface of mercury, we easily arrive at the following relation,<sup>16</sup>

$$\eta - \psi_1 = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln [H^+] + \text{constant}. \quad (1)$$

Here  $\psi_1$  denotes the average value of the potential at a distance of one ionic radius from the surface of the metal; in Stern's theory of the double layer<sup>17</sup> this quantity is identified with the electrokinetic ( $\zeta$ ) potential. The correctness of this assumption depends on the idea that the layer of the solvent, which lies nearest to the surface of the metal, is completely held by the latter, while the other layers move with the same viscosity coefficient as inside the liquid. If this assumption is not exactly fulfilled, the error will decrease with increasing dilution of the solution, because at low concentration the variation of the potential with increase of the distance from the surface beyond the limits of the

<sup>14</sup> Christiansen, *Ann. Physik*, (4), 1903, 12, 1072.

<sup>15</sup> Bruns and Frumkin, *Acta physicochimica*, 1934, 1, 232; Bruns, Frumkin, Jofa, Vanjukova and Zolotarevskaja, *ibid.*, 1938, 9, 359; Jofa and Frumkin, *C. R. Acad. Sc. U.R.S.S.*, 1938, 20, 293; Seidel, *Z. angew. Ch.*, 1935, 48, 463; Antweiler, *Z. Elektrochem.*, 1938, 44, 719, 831, 888; Stackelberg, Antweiler and Kieselbach, *ibid.*, 663; Stackelberg, *ibid.*, 1939, 45, 466.

<sup>16</sup> Frumkin, *Z. physikal. Ch. A*, 1933, 164, 121.

<sup>17</sup> Stern, *Z. Elektrochem.*, 1924, 30, 508.

Helmholtz layer proceeds very slowly. With constant values of  $i$  and  $[H^+]$ , equation (I) reduces to

$$\eta = \psi_1 + \text{constant} \quad (1a)$$

This equation enables one to explain the influence on the value of the over-voltage of the specific adsorption of the cations and anions,<sup>18</sup> this question lies, however, outside the scope of the present paper in which we limit ourselves to the simplest case, when such adsorption is not observed. From equation (1a) it is possible to interpret quantitatively the increase of the over-voltage by polyvalent cations, discovered by Herasymenko and Slendyk,<sup>19</sup> as a result of the lowering of the negative value of  $\psi_1$  due to a decrease of the diffuseness of the double layer.<sup>20</sup> When polyvalent cations are added to an acid solution the value of  $\eta$ , as can be seen from Fig. 2, increases at first and thereafter reaches a constant limiting value. If the allowable assumption is made that this limiting value of  $\eta$  corresponds to  $\psi_1 = 0$ , i.e., to a transition of the double layer into a non-diffuse state, then from measurements of the over-voltage one can determine the

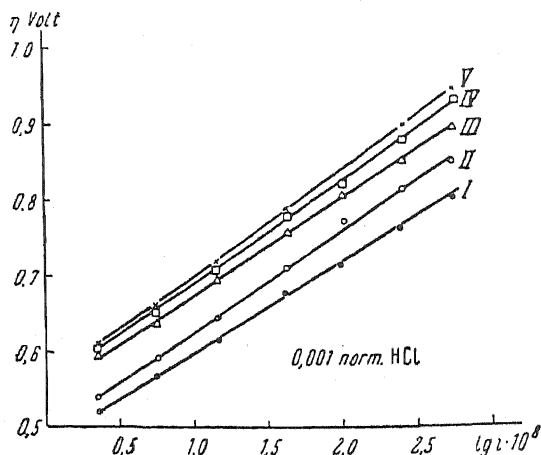


FIG. 2.—Curves for the dependence of over-voltage on the current density in  $10^{-3}$  N. HCl +  $x\text{LaCl}_3$  (Levina and Sarinsky).

(I)  $x = 0$ . (II)  $x = 10^{-6}$  N., (III)  $x = 10^{-5}$  N., (IV)  $x = 10^{-4}$  N., (V)  $x = 10^{-3}$  N.

quantity  $\psi_1$ . The values of  $\psi_1$  so found were compared with those calculated from Stern's theory, on the assumption that no specific adsorption took place and that the capacity of the Helmholtz layer was equal to  $19 \mu\text{F}/\text{cm}^2$ . The results of this calculation are shown in Fig. 3; the dependence of the potential on the concentration is seen to be in satisfactory agreement with Stern's theory, although the experimental values are always smaller in their absolute magnitude than the calculated ones; that is, the double layer has a less diffuse structure than required by Stern's theory.

Philpot<sup>21</sup> compared the value of the surface charge as determined by dropping mercury with the value calculated from Stern's theory, assuming the capacity of the Helmholtz layer to be equal to about  $23 \mu\text{F}/\text{cm}^2$  for a cationic layer and  $55 \mu\text{F}/\text{cm}^2$  for an anionic one and found a fair agreement. The method could be used for solutions as dilute as

<sup>18</sup> Jofa, Kabanow, Kuchinski and Chistyakov, *Acta Physicochimica*, 1939, 10, 317.

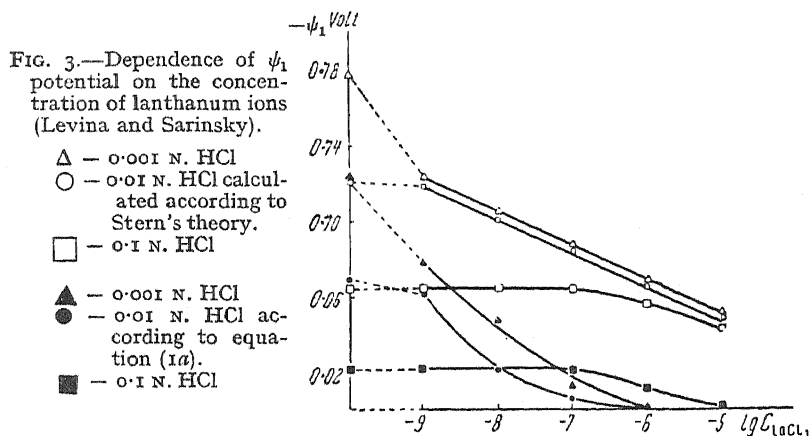
<sup>19</sup> Herasymenko and Slendyk, *Z. physikal. Ch., A*, 1930, 149, 123.

<sup>20</sup> Levina and Sarinsky, *Acta Physicochimica*, 1937, 7, 485.

<sup>21</sup> Philpot, *Phil. Mag.* (7), 1932, 13, 775.

0.001 N., and the experimental curves show in the case of dilute solutions a decrease of the capacity in the neighbourhood of the point of zero charge. However, it does not appear possible to determine quantitatively from these data the degree of diffuseness of the double layer with sufficient exactitude.

It seemed desirable to find some way of investigating the structure of the double layer by another independent method. This can be realised by measurements of the capacity of the double layer; but it is just in the case of dilute solutions, which present the greatest interest, that the measurements of the capacity are rendered difficult because of the large resistance of the solution. These difficulties have been overcome quite recently in work carried out at the Karpov Institute by Proskurnin and Worsina,<sup>22</sup> who used an alternating current with one period per second and measured the oscillations of the potential directly with the help of a short-period galvanometer. The use of an alternating current with such a low frequency enables one, with an adequate disposition of the electrodes, to carry out capacity measurements at concentrations of the order of  $10^{-3}$  N. and in acids even  $10$  N.<sup>-4</sup> The results of these measurements,



the precision of which amounts approximately to 5 %, are given in Fig. 4 taken from Worsina's paper. The ordinates give the capacity  $\mu\text{F}$  per  $\text{cm}^2$  and the abscissa—the potential measured with respect to a normal calomel electrode. It must be kept in mind that the measurements with an alternating current yield directly the value of the differential capacity  $\partial\epsilon/\partial\phi$ , where  $\epsilon$  is the charge of the mercury surface.

From the theory of Gouy and Stern it follows that the double layer is most diffuse near the point of zero charge. With increase of the absolute value of  $\epsilon$ , the ions are drawn towards the surface and the double layer passes from a diffuse to a non-diffuse structure. Accordingly, the average thickness of the double layer must have a maximum, and its capacity a minimum, at the point of zero charge. As seen from Fig. 4 the experimental curves display such a minimum neither for 1 N. nor for 0.1 N. KCl. The variation of the capacity in the neighbourhood of the zero point which is connected with a variation of the degree of diffuseness at high concentrations is completely overshadowed by those changes which take place when ions of one sign in the external side of the double layer

<sup>22</sup> Proskurnin and Worsina, *C. R. Acad. Sc. U.R.S.S.*, 1939; Worsina, *ibid.*

are replaced by ions of the other sign.\* The curve of a 0.1 N. KCl consists of two nearly horizontal portions which correspond to a double layer formed by anions ( $\partial\epsilon/\partial\phi \sim 36$ ) and by cations ( $\partial\epsilon/\partial\phi \sim 19$ ) and of a linking branch with intermediate values of the capacity; with higher positive or negative values of the charge of the surface an increase of the capacity is observed which is due to a deformation of the ions. This curve gives no indication of a diffuse structure of the double layer; on the curve corresponding to a 0.01 N. solution, however, a weak minimum appears near the point of zero charge, while on the curves corresponding to 0.001 N. and 0.0001 N. solutions this minimum, observed at  $\phi = -0.53$  (in excellent agreement with the determination of the position of the point of zero charge from electrocapillary data), becomes very marked. It seemed interesting to compare the results of these measurements with the values of  $\partial\epsilon/\partial\phi$ , calculated according to Stern's theory. If it be assumed

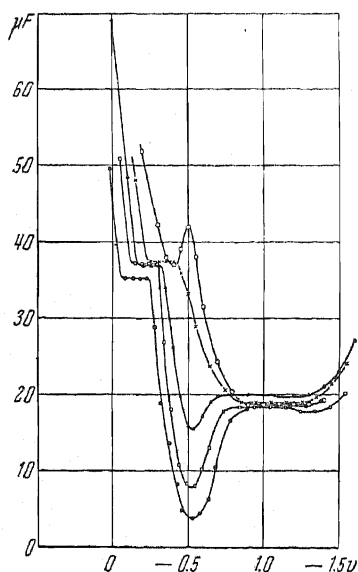


FIG. 4.—Dependence of the capacity of a mercury electrode on the concentration of the electrolyte (Proskurin and Worsina).

○ ○ ○ — 0.1 N. KCl; × × × — 0.01 N. KCl;  
 ▲ ▲ ▲ — 0.001 N. KCl;  
 □ □ □ — 0.0001 N. KCl;  
 ● ● ● — 0.0001 N. HCl.

that the anions are not specifically adsorbed and if the influence of the filling up of the surface on the adsorption be neglected, then identifying the thickness of the Helmholtz layer with the diameter of the water molecule one can put the equations of Stern's theory in the following form:<sup>16</sup>

$$\epsilon = K(\phi - \psi_1) = 2cdF \sinh \frac{\psi_1 F}{RT} + 4c\lambda F \sinh \frac{\psi_1 F}{2RT} \quad (2)$$

where  $d$  is the diameter of the water molecule ( $3.1 \times 10^{-8}$  cm.),  $\lambda$  the thickness of the ionic atmosphere for a uni-univalent electrolyte at a given concentration according to Gouy-Debye,  $K$  the capacity of the

\* On the curve of 1 N. KCl a small maximum of the quantity  $\partial\epsilon/\partial\phi$  is observed, which has already been described.<sup>23</sup> The appearance of this maximum points to a rapid intrusion of the anions into the surface layer near the point of zero charge with a decrease of the cathodic polarisation, connected perhaps with the existence of Van der Waals' forces between the adsorbed anions which decrease their electrostatic repulsion.

<sup>23</sup> Proskurnin and Borissowa, *Acta Physicochimica*, 1936, 4, 819.

non-diffuse layer, and  $c$  the concentration expressed in g. eq. per cm.<sup>3</sup> The first term of the right hand part of equation (2) expresses, as is well known, the charge of the non-diffuse, and the second one that of the diffuse portion of the double layer. Equation (2) cannot, however, be used for the calculation of  $\partial\epsilon/\partial\phi$  or for comparison of the value obtained with the experimental data within the whole accessible potential range, since it implies the constancy of the quantity  $K$  for all values of  $\phi$ , whereas, in reality the values of  $K$  for a positively and negatively charged surface are certainly different. I have, therefore, attempted, as it has already been done by Philpot, to modify equation (2) by introducing two values for the capacity of the Helmholtz layer  $K_1$  and  $K_2$ , corresponding to a double layer formed by anions and by cations respectively. Under such conditions the quantity  $K$  in equation (2) must be treated as a variable, depending on the concentration of the anions and of the cations in the Helmholtz layer. Since these concentrations are proportional to  $\exp. \frac{\psi_1 F}{RT}$  and to  $\exp. \left(\frac{-\psi_1 F}{RT}\right)$  respectively, it is natural to define the quantity  $K$  by the equation

$$K = \frac{K_1 \exp. \frac{\psi_1 F}{RT} + K_2 \exp. \left(\frac{-\psi_1 F}{RT}\right)}{\exp. \frac{\psi_1 F}{RT} + \exp. \left(\frac{-\psi_1 F}{RT}\right)} \quad (3)$$

The physical meaning of equation (3) is that of a Helmholtz layer consisting of two parallel condensers charged to the same potential  $\phi - \psi_1$ . Philpot uses another method of linking both branches of the curve which apparently does not correspond to a definite physical picture. If this value of  $K$  is substituted in equation (2) then the following relations are readily obtained:

$$\phi = \psi_1 + \frac{2cdF}{K} \sinh \frac{\psi_1 F}{RT} + \frac{4c\lambda F}{K} \sinh \frac{\psi_1 F}{2RT} \quad (4)$$

$$\frac{\partial\epsilon}{\partial\phi} = KA \left\{ A + K - \frac{1}{2} (K_1 - K_2) \frac{(\phi - \psi_1) F}{RT} \cosh^{-2} \frac{\psi_1 F}{RT} \right\} \quad (5)$$

where 
$$A = \frac{2cF^2}{RT} \left( d \cosh \frac{\psi_1 F}{RT} + \lambda \cosh \frac{\psi_1 F}{2RT} \right).$$

From the equations (4), (5) and (3) it is easy to plot a curve which gives the value of the capacity  $\partial\epsilon/\partial\phi$  as a function of  $\phi$ . In this way the curves of Fig. 5 were calculated for concentrations varying from 0.1 to 0.0001 N. with  $K_1 = 38$  and  $K_2 = 20 \mu F/\text{cm.}^2$  (the abscissae are reckoned from the point of zero charge). As seen from a comparison of Figs. 4 and 5 the general disposition and the shape of the curves calculated from Stern's theory is very similar to that of the experimental curves. The calculated values of the capacity lie, however, much lower than the observed ones; thus, the smallest observed value of the capacity for a 0.0001 N. solution is equal to 3.9, whereas calculation from equation (5) yields  $\partial\epsilon/\partial\phi = 2.15$ , and according to Gouy's theory of the diffuse layer  $2.36 \mu F$  per cm.<sup>2</sup>. This confirms the conclusion derived from overvoltage data, according to which the real double layer is less diffuse than would be expected theoretically. This discrepancy points to the existence of specific (*i.e.*, independent of the charge), attractive forces between the surface of the metal and the ions. This adsorption effect cannot, however, be identical



with that which is observed at higher concentrations. In fact an excessive capacity is observed on both sides of the point of zero charge, *i.e.*, the above interaction must be ascribed both to cations and anions, whereas, as is well known from electrocapillary data the inorganic cations display at higher concentrations a negative and not a positive adsorption.<sup>24</sup> We are thus forced to the assumption that we have to do here with an attraction which, at very small distances, is replaced by repulsion. It is possible that at large distances the image forces postulated by Gurney<sup>25</sup> come into play, but that, for some hitherto unknown reason, they are not observed when the ions are in a close vicinity to the surface of the mercury electrode. We thus see that the deviations from Stern's theory observed experimentally cannot be removed by the introduction of a specific adsorption potential for the ions in the form advanced by the author of this theory. We cannot therefore directly use Stern's theory for the calculation of  $\psi_1$ —potentials in which we are particularly interested. These values can, however, be obtained from the experimental values of the capacity if one assumption of Stern's theory only

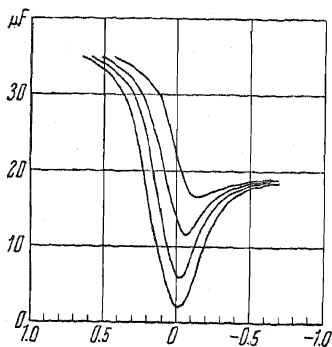


FIG. 5.—Dependence of the capacity on the concentration of the electrolyte according to Stern's theory.

(0.1, 0.01, 0.001 and 0.0001 N. solutions.)

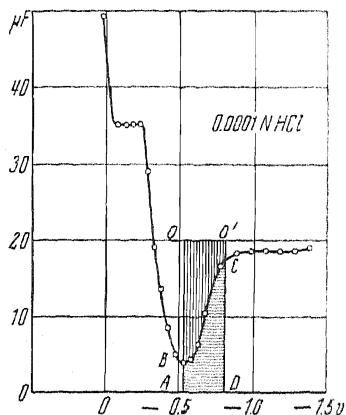


FIG. 6.—Calculation of the  $\psi_1$  potential from the experimental data of the electrode capacity.

is preserved, namely, that the Helmholtz double layer has a constant capacity. This assumption which, as has been pointed out above, does not hold for the entire curve is certainly valid for a part of it, corresponding to not too large and not too small negative charges of the surface (Helmholtz layer with undeformed cations), because in this range the experimental values of  $\partial\epsilon/\partial\phi$  at higher concentrations as seen from Fig. 4, actually show a satisfactory constancy. In dilute solutions it is thus possible to apply to this part of the curve the first equation of Stern's theory

$$\epsilon = K(\phi - \psi_1) \quad (6)$$

the derivation of which does not imply any assumptions beyond that of the constancy of the capacity in the Helmholtz layer. Inasmuch as the measurements of the capacity in dilute solutions enable one to find the value of the potential corresponding to  $\epsilon = 0$  and the quantity  $\partial\epsilon/\partial\phi$ , we can thus find the value of  $\epsilon$  for any  $\phi$ ; it is determined by the area

<sup>24</sup> Frumkin, *Sov. Phys.*, 1933, 4, 364.

<sup>25</sup> Gurney, *Proc. Roy. Soc., A*, 1931, 134, 144.

ABCD (Fig. 6). If AO is equal to  $K$ , then the area BOO'C divided by  $K$  gives, according to equation (6), the quantity  $\psi_1$ . This simple graphical calculation of the quantity  $\psi_1$  implies the knowledge of the quantity  $K$ , which can be found from the experimental curve for  $\partial\epsilon/\partial\phi$  as the limit to which this quantity tends with increase of  $\phi$ . With that precision of the measurements which has been realised hitherto, the quantity  $K$  can be determined but approximately; the determination of the  $\psi_1$ -potential by the method described becomes therefore inexact as soon as the observed values of  $\partial\epsilon/\partial\phi$  do not vary much with the potential. In that part of the curve where the value of  $\partial\epsilon/\partial\phi$  is still markedly lower as compared with its limiting value, a certain degree of arbitrariness in the choice of the value  $K$  hardly influences the result of the calculation of  $\psi_1$ . Thus at 0.001 N. and  $\phi = -0.73$  (0.2 from the point of zero charge on the cathode side) the above method of calculation yields  $\psi_1 = -0.067$  with  $K = 20$  and  $\psi_1 = -0.06$  with  $K = 19$ . According to Stern's theory at this value of the potential with  $K = 20$ , we should have  $\psi_1 = -0.11$ . It seemed very interesting to compare these values of  $\psi_1$  with those obtained from equation (1a) from overvoltage data. Unfortunately, the value  $\phi = -0.73$  at  $c = 0.001$  N. corresponds to a value of  $\eta$  equal to 0.28 only, whereas the measurements of Levina and Sarinsky<sup>20</sup> begin with  $\eta = 0.52$ , and our calculations of  $\psi_1$  are no longer reliable for more negative values of  $\phi$ . If the overvoltage curves obtained by Levina and Sarinsky are extrapolated to  $\eta = 0.28$  then, by comparison of the overvoltages observed in pure HCl and in the of presence an excess of  $\text{LaCl}_3$ , one gets  $\psi_1 = -0.06$ , in good agreement with the results of capacity measurements. We give in Table I a few more values obtained for  $\psi_1$  from (6) for 0.0001 N. HCl, assuming  $K = 20$ , and the corresponding values calculated according to Stern's theory. The potentials are reckoned not with respect to the normal electrode but from the point of zero charge.

TABLE I.  
( $10^{-4}$  N. HCl.  $K = 20$ .)

	$\psi_1$ According to Equation (6).	$\psi_1$ According to Stern's Theory.
- 0.1	- 0.076	- 0.085
- 0.2	- 0.123	- 0.147
- 0.3	- 0.141	- 0.177

The coincidence of the results of the determination of the value of  $\psi_1$  according to the capacity curves and to the overvoltage, although not yet tested on a sufficiently large experimental material, forces us to consider these values of  $\psi_1$  as sufficiently reliable. The values of the  $\zeta$ -potential given in the literature and obtained from electrokinetic data, usually lie somewhat lower than the values  $\psi_1$  calculated by us; this could be explained by the insufficient exactness of the assumptions underlying the theory of electrokinetic phenomena; the values obtained recently for glass by Rutgers, Verlende and Moorkens,<sup>26</sup> with due account for the surface conductivity are, however, very close to those given here.

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<sup>26</sup> Rutgers, Verlende and Moorkens, *Proc. Kon. Ak. Wet. Amsterdam*, 1938, 41, 763.

# SOME OBSERVATIONS ON THE DOUBLE LAYER CAPACITY AT MERCURY ELECTRODES.

BY I. M. BARCLAY AND J. A. V. BUTLER.

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We begin with some remarks on previous determinations of the double layer capacity of electrodes, which have been made by the following methods:

(1) From the electrocapillary curves, by the original theory of Helmholtz, according to which

$$\frac{d\rho}{dV} = -e; \quad \frac{d^2\rho}{dV^2} = K$$

where  $\rho$  is the surface tension of the metal-solution interface,  $e$  is the charge on either side of the double layer, and  $K$  the capacity of unit area. Gouy found<sup>1</sup> in this way a minimum capacity of about  $17 \mu\text{F./cm.}^2$  for mercury electrodes in salt solutions. The values actually recorded by Gouy refer mostly to concentrated solutions and Gouy's electrocapillary curves are not given in a form which facilitates the calculation of capacity. Fig. 1 shows some values of  $e$  obtained from accurate

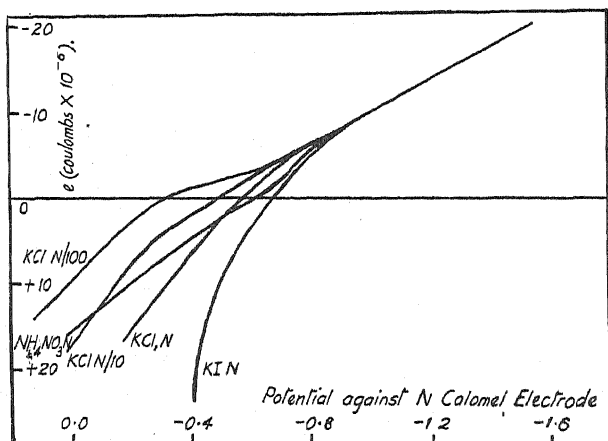


FIG. 1.— Charge on mercury calculated from electrocapillary curves.

electrocapillary curves determined by Wightman,<sup>2</sup> which have not previously been published. The capacity in the right hand (negative) branch of the curve, which is the same in all cases is  $16$  to  $17 \mu\text{F./cm.}^2$ . After a transition stage in which the capacity may fall to comparatively small values in the region of the maximum of the electrocapillary curve, it becomes approximately constant again with values which depend markedly on the nature of the electrolyte, e.g. for  $\text{KCl N./l.}$   $42 \mu\text{F./cm.}^2$ ; for  $\text{NH}_4\text{NO}_3 \text{ N./l.}$  about  $30 \mu\text{F./cm.}^2$ ; for  $\text{Na}_2\text{SO}_4 \text{ N./l.}$   $34 \mu\text{F./cm.}^2$ . At the extreme left the capacity begins to rise again.

<sup>1</sup> *Ann. Chim. Physique*, 1903, **29**, 159; 1917, **7**, 129.

<sup>2</sup> *Cf. J. physical Chem.*, 1931, **35**, 3293.

(2) By measuring the flow of current required to keep the potential of an expanding mercury surface constant. By this method L. St. J. Philpot obtained<sup>3</sup> curves similar to Fig. 1, and gave the values shown in Table I.

TABLE I.

	Negative Branch.	Positive Branch.
HCl .	23.3 $\mu\text{F}$	53.7 $\mu\text{F}$
NaCl	23.6 $\mu\text{F}$	57.3 $\mu\text{F}$

(3) By direct charging experiments. If it is assumed that no charges cross the double layer, the increase of charge of each side when a current  $i$  flows for a time  $dt$  is  $dq = idt$ , and if the consequent increase of the p.d. is  $dV$ , the capacity is  $K = idt/dV$ . By this method, Bowden and Rideal<sup>4</sup> found values of about 6  $\mu\text{F}/\text{cm}^2$  for the regions between the reversible hydrogen electrode and the hydrogen overvoltage of mercury. In more recent experiments with protected mercury surfaces<sup>5</sup> the value of 20  $\mu\text{F}/\text{cm}^2$ , which agrees with that derived from electrocapillary curves has been obtained.

(4) By the use of alternating current in a capacity bridge. Originally employed by Krüger,<sup>6</sup> who obtained values of 7 to 10  $\mu\text{F}/\text{cm}^2$ , this method was used by Frumkin and Proskurnin,<sup>7</sup> who taking special precautions to prevent the contamination of the surface with grease, etc., found a minimum capacity of about 20  $\mu\text{F}/\text{cm}^2$ , and by Borissowa and Proskurnin.<sup>7(a)</sup>

Various types of double layers have been suggested in order to account for these values.

(1) *The Helmholtz double layer*,<sup>8</sup> consisting of two layers of charges facing each other at a constant distance like the plates of a condenser. The capacity is  $e/V = D/4\pi\delta$ , where  $D = d.c.$ ;  $\delta$  = distance between the plates. Gouy's value of the minimum capacity requires

$$\delta = 0.3 \times 10^{-8} \text{ cm.}$$

which was recognised as unreasonably small.

(2) *The Gouy diffuse layer*,<sup>9</sup> in which the ions are distributed in a way which satisfies Poisson's and Boltzmann's equations. Assuming no limit to the nearness of approach of ions to the surface, this gives capacities of the order of 240  $\mu\text{F}$ .

(3) *The Stern double layer*,<sup>10</sup> which combines the salient features of both of the former, by assuming that adsorbed ions form a Helmholtz layer to which a diffuse Gouy layer is added.<sup>11</sup> It is capable of accounting for the general features of the curves (e.g. Fig. 1) and the results of Philpot's experiments.

(4) *Adsorbed dipoles* must now be recognised as contributing an important element of the potential difference. When platinum electrodes are forced from the region of hydrogen to that of oxygen evolution, linear changes of the potential with time were observed by Bowden,<sup>12</sup> who attributed them to the desorption of hydrogen and adsorption of

<sup>3</sup> *Phil. Mag.*, 1932, 13, 775.

<sup>4</sup> *Proc. Roy. Soc., A*, 1928, 120, 59.

<sup>5</sup> Bowden and Grew, quoted in *Ann. Rep. C.S.*, 1938, 112.

<sup>6</sup> *Z. physikal. Chem.*, 1903, 45, 1.

<sup>7</sup> *Trans. Faraday Soc.*, 1934, 31, 110.

<sup>7(a)</sup> *Acta Physicochim.*, 1936, 4, 819.

<sup>8</sup> *Wied. Ann.*, 1879, 7, 337.

<sup>9</sup> *Compt. rend.*, 1909, 149, 654; *Ann. Physique*, 1917, 7, 129; cf. Chapman, *Phil. Mag.*, 1913, 25, 475.

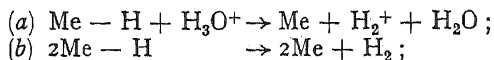
<sup>10</sup> *Z. f. Elektrochem.*, 1924, 30, 508.

<sup>11</sup> Cf. Müller, *Kolloid-chem. Beih.*, 1928, 26, 257.

<sup>12</sup> *Proc. Roy. Soc. A*, 1929, 125, 445.

oxygen. Butler and Armstrong<sup>13</sup> found that the capacity of platinum electrodes in the anodic region can have any value between two limits, which are observed respectively with (1) an oxygen saturated surface, produced by previous anodic polarisation; (2) a clear surface produced by the reduction of the former. Values of 100 and 1200  $\mu\text{F.}$  were observed in these cases with a platinum electrode having an apparent area of 1  $\text{cm.}^2$ . Similar effects have been observed<sup>14</sup> with platinum in the cathodic region, and it has been shown that adsorbed hydrogen may be deposited on the electrode below the reversible hydrogen potential, and the electrode potential varies linearly with the amount of adsorbed hydrogen. Frumkin and his associates have obtained results under rather different experimental circumstances.<sup>15</sup>

The object of these experiments was to study further the capacity of mercury electrodes and particularly to ascertain whether any evidence could be obtained of the deposition of adsorbed hydrogen. This was particularly desirable, since it has been suggested that the first stage in the liberation of hydrogen is always the formation of adsorbed hydrogen. According to Horiuti and Okomato,<sup>16</sup> this is followed by one of two alternative processes:



and they suggested, on the basis of the hydrogen-deuterium separation coefficients that the process is (a) with Ag, Ni, Pt, Au, Cu, Pb (alkali); and (b) with Hg, Sn and Pb (acid). They have given some oscillograms,<sup>17</sup> which they regard as indicating the existence of molecular hydrogen ions on mercury electrodes.

No direct evidence has hitherto been obtained of the deposition of hydrogen on mercury electrodes at potentials below the usual hydrogen overvoltage. This might easily have escaped observation in the experiments previously made, since in these experiments the mercury has been initially at or near the reversible hydrogen potential, and it is quite possible that in these circumstances an adsorbed film of hydrogen would be already present. With mercury it is impossible to free the surface from hydrogen by anodic polarisation, as this would cause the solution of the mercury. Our object was, therefore, to create a new mercury surface and to polarise it cathodically as soon as possible after its formation.

We used a cathode ray oscillograph, with suitable amplifiers to record the charging curves. With this, comparatively large currents could be employed, and the charging process took times of the order of  $10^{-2}$  to  $10^{-3}$  seconds. The solutions were initially freed from oxygen by bubbling purified nitrogen at a reduced pressure, but traces of oxygen had no perceptible effect at these speeds. Some typical records are shown in Fig. 2 (Plate 1). In hydrochloric and sulphuric acids, the charging curve consists of two approximately linear portions, with a change of direction at about  $E_h = -0.3$ . The area of the mercury was estimated at about 2  $\text{cm.}^2$ . It could not be exactly measured, and probably varied a little from one experiment to another. Table II. gives the

<sup>13</sup> *Proc. Roy. Soc. A*, 1929, **137**, 504; 1933, **143**, 89; also Butler and Drever, *Trans. Faraday Soc.*, 1936, **32**, 427.

<sup>14</sup> Pearson and Butler, *ibid.*, 1938, **34**, 1163.

<sup>15</sup> Cf. Ershler and Frumkin, *ibid.*, 1939, **35**, 464.

<sup>16</sup> *Sci. Pap., I. Phys. Chem. Res. Tokyo*, 1936, **28**, 231; **29**, 223.

<sup>17</sup> *Bull. Chem. Soc. Japan*, 1938, **13**, 228.

average values of the capacity in the two branches in a considerable number of experiments. They are of the same order as those observed by Philpot; and if the area of the electrode is taken as rather greater than 2 cm.<sup>2</sup>, they will be in excellent agreement with the figures derived from the electrocapillary curves. This is the first time that the initial stage with the greater capacity has been directly observed in charging experiments and the results of three methods, *viz.*, calculation from the electrocapillary curve, flow of current to an expanding surface and direct charging, are now in substantial agreement.

TABLE II.—CAPACITIES OF A MERCURY ELECTRODE, AREA *ca.* 2 CM.<sup>2</sup>  
(COULOMBS  $\times 10^{-6}$ /VOLTS).

Electrolyte.	Surface.	Capacity.		Ratio.	Number.
		Stage 1.	Stage 2.		
N HCl . . .	New	108	44.7	2.42	16
	Old	104	45.0	2.31	15
N H <sub>2</sub> SO <sub>4</sub> . .	New	104	47.8	2.25	20
	Old	100	45.9	2.18	11

It is clear that there is no evidence of the deposition of hydrogen on the electrode at any potential between the initial potential of mercury in the solution, and that at which hydrogen is continuously liberated. The experiments also give a comparison of the behaviour of (1) new surfaces, and (2) old surfaces, at which hydrogen had been liberated and the overvoltage then allowed to decay. No appreciable differences in the two cases were found, and there is thus no evidence of the formation of adsorbed hydrogen during its liberation in a form which persists during the decay of the overvoltage.

### Experimental.

The experimental vessel is shown in Fig. 3. The desiderata were a complete absence of taps in any position from which grease could be communicated either to the mercury or the solution, and a means of making fresh mercury surfaces. The tube (T) supplying the mercury was surrounded by a collar C inside which the mercury electrode was formed. When the collar was raised by winding the supporting threads S, the pool of mercury within the collar escaped through the hole H. A fresh pool was made by applying pressure to the reservoir R. The solution was freed from air in the vessel V, from which it could be blown into the cell by gas pressure. The whole apparatus could be freed from air initially by circulating purified nitrogen.

Experiments were also made with more dilute HCl solutions. In 0.1 N. HCl, the oscillograms were very similar to those described above. In 0.01 N. HCl (Fig. 2c) the ohmic potential fall between the electrode and the tip of the reference electrode caused an initial rapid change of potential. In this solution the curve was abnormally flat at the beginning, but the total length is of the same order as previously.

### Effect of Capillary Active Substances.

The effect of organic substances on the capacity has been investigated by Gorodezkaya and Frumkin,<sup>18</sup> who found that cetyl alcohol, palmitic

<sup>18</sup> C. R. de l'Ac. des Sci. de U.R.S.S., 1938, 18, 639.

and oleic acids reduce the capacity considerably in the range of potential difference in which the electrocapillary curves show them to be adsorbed.

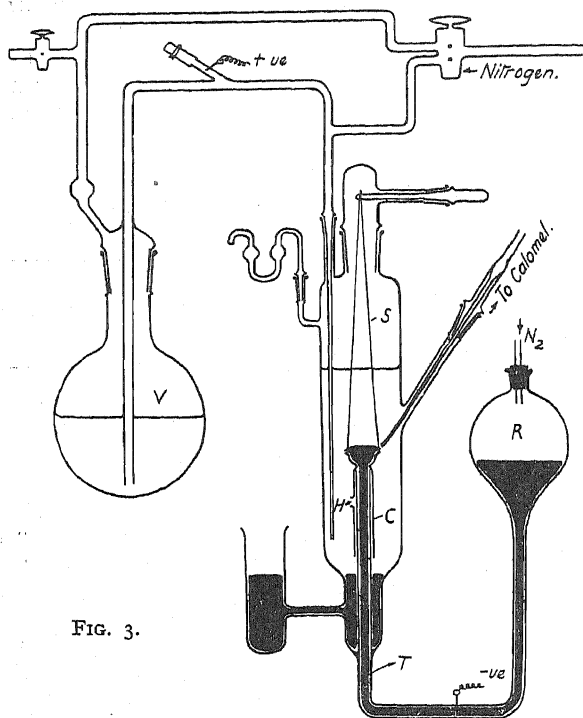


FIG. 3.

We made experiments with additions of *t*-amyl alcohol and tetra-ethyl ammonium chloride. The former produced very curious changes in the shape of the charging curves (Fig. 4). As its concentration is increased two flat stages appeared in the initial and final portions of the curve respectively, while between these the "capacity curve" becomes gradually steeper. The decrease of the capacity in this region is evidently due to the adsorption of the alcohol, and a curve which closely resembles the adsorption isotherm is obtained

by plotting the capacity against the concentration (Fig. 5). The significance of the flatter parts of the curve is not clear.

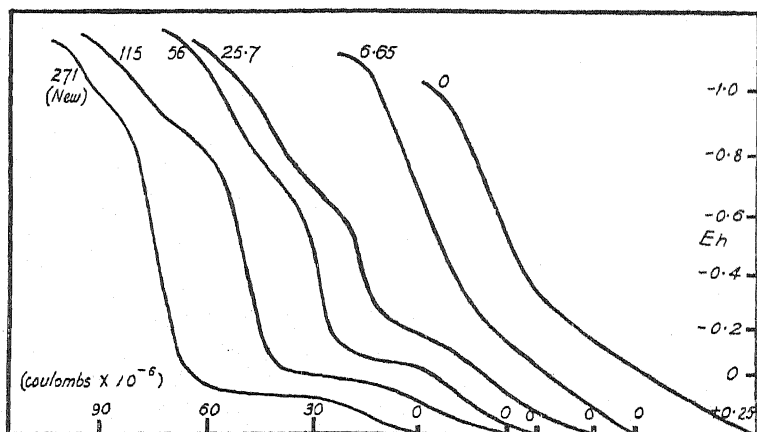


FIG. 4.—Oscillograms obtained with HCl in presence of Amyl Alcohol.

The oscillograms are unaltered by the tetra-ethylammonium salt, except for a flattening at the extreme upper end (Fig. 2d). In this case

the electrocapillary curves<sup>19</sup> show that practically no adsorption occurs at the initial potential of the unpolarised mercury, but adsorption takes place at the more negative potentials. This is confirmed by the absence of any reduction of the capacity in the initial parts of the curve. The oscillogram is taken so rapidly that one could hardly expect adsorption equilibrium to keep pace with the potential changes; but the flattening of the upper end is probably due to the adsorption here of tetra-ethyl-ammonium ions.

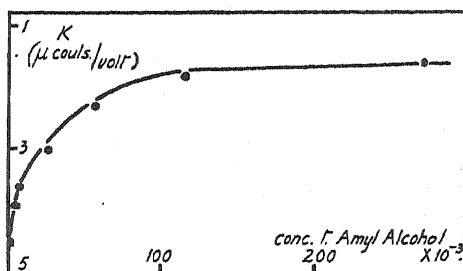


FIG. 5.—Variation of capacity of a mercury electrode with conc. of *t*-amyl alcohol.

### Summary.

1. Oscillograms of the negative polarisation of freshly made mercury surfaces show two stages (1) the more positive region ( $E_h > -0.3$ ) in which the capacity is of the order of  $50 \mu\text{F./cm.}^2$ ; (2) the more negative region in which it is about  $22 \mu\text{F./cm.}^2$ . Stage (1) has now been observed for the first time in direct charging curves, which are now in substantial agreement with the results of the electrocapillary calculations and experiments with expanding mercury surfaces.

2. There is no evidence that the deposition of adsorbed hydrogen occurs at any potential below that at which hydrogen is continuously evolved, which is postulated in some recent theories of overvoltage.

We thank the Government Grant Committee of the Royal Society for a grant, out of which the oscillograph was purchased, and the Carnegie Trustees for a Scholarship granted to I.M.B.

<sup>19</sup> *Proc. Roy. Soc., A*, 1929, **122**, 399.

## RELAXATION EFFECTS IN THE DOUBLE LAYER. CATAPHORESIS; DIELECTRIC CONSTANT.

By J. J. HERMANS.\*

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It is generally assumed that the particles in a colloid or suspension are surrounded by an electric double layer which extends over a certain distance. As regards the diffuse part of the double layer, this distance is chiefly determined by the concentration of the surrounding electrolytes. It is well known that in those cases where the Debye-Hückel approximation applies the "thickness" of the double layer is equal to  $1/\kappa$ , the characteristic length of the Debye-Hückel theory which is proportional to the reciprocal square root of the electrolytic concentration. Properly speaking,  $1/\kappa$  is the distance from the surface of the particle where the potential has dropped to about  $1/e$  its value on the surface. In the

\* Netherlands Fellow of the Ramsay Memorial Fellowship Trust.



present paper both the particle and its double layer are supposed to show spherical symmetry. Using  $1/\kappa$  as a measure for the thickness of the double layer, and denoting the radius of the particle by  $R_0$ , it will then be obvious that  $\kappa R_0$  represents a (dimensionless) quantity which determines the ratio between the dimensions of the particle and those of the double layer: If  $\kappa R_0 \gg 1$  the double layer is thin compared with the particle, if  $\kappa R_0 \ll 1$  the double layer is diffuse compared with the particle size.

If now the particle acquires a velocity with respect to the solvent, the diffuse double layer loses its spherical symmetry. For, as a result of the finite relaxation time of the ions in the double layer, these ions only partly succeed in "keeping pace with the particle." This relaxation effect is well-known from Onsager's theory of electrolytic conductivity. In this theory, however, the distribution of charges round a given ion is calculated on the assumption that each ion moves in a liquid at rest, *i.e.*, the influence of the flow of liquid round an ion on the distribution of the surrounding ions is neglected. This may be permissible for ions, but it certainly does not apply to particles of colloidal dimensions. In the special case where  $\kappa R_0 \gg 1$ , the particle will often carry along its double layer almost entirely, thus reducing the effect of relaxation considerably. The way in which the theory of relaxation is to be extended will become clear below.

Of the various cases where the distortion of the double layer plays a part we may mention the motion in a gravitational or in a sonic field.<sup>1</sup> However, the most interesting application made at present is that to the motion in an external electric field. This also represents a more complicated phenomenon, since the flow of the liquid in an electric field is determined by the distribution of the charges in the double layer. Conversely, however, this distribution is determined by the flow of liquid. A complete theory should therefore treat the hydrodynamic equations and the differential equations of relaxation simultaneously. For the present we resort to the following obvious approximation: The flow of liquid which applies to a spherical distribution of charges and the resulting resistance experienced by the sphere are taken as zero order approximation. For this flow of liquid the distortion of the double layer and the corresponding electric force on the sphere are calculated, while the correction which should be made in the hydrodynamic equations of the surrounding liquid are left out of account. From the results obtained it can be shown that this method only applies to insulating particles and there only if  $\kappa R_0 \gg 1$ . For  $\kappa R_0 \approx 1$  the relative error becomes of the order of 100 per cent., and for  $\kappa R_0 \ll 1$  the method fails altogether. This latter case, however, hardly ever occurs in practice, since in the determination of cataphoretic velocity the particle is usually so large that no electrolytic concentration exists where  $\kappa R \ll 1$ , unless we are dealing with solvents other than water.

Before proceeding to give an outline of the theory, it may be mentioned that in Komagata's<sup>2</sup> calculations the procedure is reversed. This author calculates the distribution of charges round the moving particle under the (taeid) assumption that the influence of hydrodynamic flow can be neglected. The charge density thus found is substituted in the hydrodynamic differential equations, and the resistance calculated in the

<sup>1</sup> J. J. Hermans, *Phil. Mag.* (7), 1938, **25**, 426; 1938, **26**, 674.

<sup>2</sup> S. Komagata, *Res. electrotechn. Lab. Tokyo*, No. 387, Sept. 1935.

usual way. This method is not applicable if  $\kappa R_0 \gg 1$ . It can further be shown that it also fails in the intermediate region  $\kappa R_0 \approx 1$ , where the relative error produced by the approximation is of the order of 100 per cent. In the extreme case where  $\kappa R_0 \ll 1$ , Komagata's method is better than ours.

The purpose of this paper is to give as accurate a survey as possible without going into mathematical details. Special mention will be made of the various assumptions which underly the theory. One of these assumptions has already been mentioned, *viz.* :

(a) The particle is a sphere. Many conclusions will in principle also apply to non-spherical particles, but an accurate mathematical treatment is then impossible. We may at once add the following further assumptions :

(b) The double layer is thin compared with the particle radius, and

(c) The particle is an insulator. For, although Henry<sup>3</sup> derived formulæ for the cataphoretic velocity of conducting particles and also for a particle radius which is of the same or of lower order than the thickness of the double layer, it has already been mentioned that in these cases the relaxation causes Henry's theory to break down (compare below). While assumptions (b) and (c) are necessitated by the theory of relaxation, the following six assumptions are already inherent to Henry's theory of cataphoresis :

(d) Stokes's hydrodynamic equations apply, *i.e.*, the so-called inertia terms may be neglected. This will hold good in those cases where the external field is sufficiently small.

(e) These equations also apply in the double layer. The viscosity  $\eta$  and the dielectric constant  $D$  are supposed to be the same as those in the bulk of the liquid.

(f) The electric potential round the particle at rest has spherical symmetry.

(g) The electric potential of the external field is merely superposed on that of the double layer.

(h) There is no slip at the surface of the particle. This assumption is well founded in those cases where an ordinary velocity gradient exists. In an external electric field, however, the velocity gradient in the immediate neighbourhood of the particle is of the same order as the potential gradient in the double layer and much larger than that which occurs in "ordinary" flow of liquid.

In addition, an assumption is made which is usually not mentioned explicitly, *viz.* :

(j) What is called the surface of the particle in a hydrodynamic sense is a sphere, with radius  $R$ , say. This is evident if the hydrodynamic surface coincides with that of the particle itself ( $R = R_0$ ), but in many cases the surface may behave in a way which is very different from that of a smooth surface. If, for instance, the surface consists of a hydrophilic substance, complications may occur in the double layer, for which ordinary hydrodynamics do not account.

If all these assumptions are taken for granted and the equations of motion solved accordingly, the resistance experienced by the sphere becomes :<sup>3</sup>

$$W = eE + 6\pi\eta RU - \frac{3}{2}RDE\xi, \quad . \quad . \quad . \quad (1)$$

<sup>3</sup> D. C. Henry, *Proc. Roy. Soc., A*, 1931, **133**, 106.

where  $E$  is the external field,  $U$  the cataphoretic velocity,  $e$  the charge of the particle and  $\zeta$  its electrokinetic potential. For uniform velocity this resistance equals the force  $eE$  exerted on the particle by the electric field; in other words

$$eE + 6\pi\eta RU - \frac{2}{3}RDE\zeta - eE = 0. \quad (2)$$

Now, the charge  $e$  is related to the  $\zeta$ -potential:

$$e = \kappa R^2 D \zeta. \quad (3)$$

This relation assumes the Debye-Hückel approximation to be applicable, but it will give the right order of magnitude in other cases as well. The term  $eE$  in (2) is therefore of the order of  $\kappa R$  times the other terms, which means that the total force on the particle is the difference between two forces which are large compared with the resulting force itself. Consequently, a relative error  $\xi$  in the equations of motion may lead to a relative error of the order of  $\kappa R \xi$  in the cataphoretic velocity.

So far all relaxation has been neglected. The general theory of this effect may be briefly sketched as follows. Let  $f_K$  be the number of ions with charge  $e_K$  per unit of volume in the double layer;  $f_K \rightarrow n_K$  for large distance from the particle. The potential  $\psi$  in a given point conforms to Poisson's equation

$$\Delta\psi = -\frac{4\pi}{D} \sum f_K e_K. \quad (4)$$

Three factors will tend to change  $f_K$ : (i) the diffusion, (ii) the electric force  $e_K \text{ grad } \psi$  on the ion considered, (iii) the velocity  $q$  of the liquid with respect to the particle. This gives

$$\frac{\partial f_K}{\partial t} = \frac{kT}{\rho_K} \Delta f_K + \frac{e_K}{\rho_K} \text{div} (f_K \text{ grad } \psi) - \text{div} (f_K q). \quad (5)$$

where  $kT/\rho_K$  represents the diffusion constant of the ion concerned and is proportional to the mobility. The term  $\text{div} (f_K q)$  represents the influence of the streaming, and is neglected in Onsager's theory of electrolytic conductivity. The potential  $\psi$  is the total potential, i.e., it contains that of the external field  $E$ . It is obvious that there are as many equations (5) as there are ionic species. The expression for  $\partial f_K/\partial t$  is zero if the motion is uniform, which gives

$$kT \Delta f_K + e_K \text{div} (f_K \text{ grad } \psi) - \rho_K \text{div} (f_K q) = 0. \quad (6)$$

Together with (4) these equations determine the problem to be solved.

In the expression (5) for  $\partial f_K/\partial t$  it is assumed that:

(k) The Brownian movement of the particle may be neglected compared with that of the ions. Apart from this assumption the equation is as general as it could possibly be. It is only when solving the system (4, 6) that further assumptions must be made, viz.:

(l) For  $q$  we may substitute the value found by Henry<sup>3</sup> for a charge distribution with spherical symmetry. As has already been mentioned, this means a relative error of the order of  $1/\kappa R$  in the cataphoretic velocity (see also below).

(m) The Debye-Hückel approximation applies, which means that the potential and therefore  $\zeta$  must be small ( $\zeta < 50$  mV., say). This obviously further implies the assumption that the diffuse part of the double layer is the only one responsible for relaxation.



be different from the electro-osmotic velocity along a plane wall consisting of the same material, even if the  $\zeta$ -potential is independent of the curvature. Further, the relaxation and therefore the cataphoretic velocity will depend on the shape of the particle, although it is at present impossible to say to what extent this will be so.

The magnitude of the corrections is surprisingly high. For particles with  $\zeta = 50$  mV. in a non-symmetrical electrolyte the correction amounts to more than 100 per cent. To a certain extent this result may be due to the application of Debye-Hückel's approximation. It is hardly to be expected, however, that a more accurate theory would lead to a different order of magnitude.

A few words may be said finally about the influence of the relaxation on the dielectric constant of the systems concerned.<sup>6</sup> Each particle with its distorted double layer represents a dipole, which can easily be calculated from the extra charge density  $S$  in the volume elements of the surrounding liquid. Multiplying with the number of particles per unit of volume one obtains the polarisation per unit of volume. For the special case of low frequency this leads to a simple formula for the dielectric constant  $D'$  of the system, which will be given in terms of the relative increase:

$$\frac{D' - D}{D} = \left\{ -\frac{9}{4} \frac{\sum n_K e_K^3}{\sum n_K e_K^2} + \frac{5}{4} \frac{D\zeta}{4\pi\eta} \frac{\sum n_K e_K^2 \rho_K}{\sum n_K e_K^2} \right\} \frac{\zeta}{\kappa R} \frac{p}{kT} \quad (10)$$

where  $p = 4/3\pi R^3 n$  is the volume concentration of the dispersed substance. Obviously the difference between  $D$  and  $D'$  decreases if the electrolytic concentration is increased. For (10) to be applicable, the assumptions mentioned in the discussion of cataphoresis must hold good; in particular:  $\kappa R \gg 1$ . For large values of  $\kappa R$ , however, the difference between  $D$  and  $D'$  becomes so small that the formula loses its practical interest. We therefore apply (10) to the intermediate region  $\kappa R \approx 1$ , where it only gives the order of magnitude. Doing so we find, with a  $\zeta$ -potential of about 50 mV., the following result:

$$\frac{D' - D}{D} \approx \text{a few times } p.$$

In other words, we may expect a relative change of 1 per cent. in the dielectric constant if the volume concentration is of the order of 1 per cent.

Unfortunately the deformation of the double layer is only one out of several factors. In many cases the effect of diluting the solvent with a substance of lower or higher dielectric constant will in itself produce a change of the same order.<sup>7</sup> Further, hydration will tend<sup>8</sup> to decrease  $D$ , and it will not always be possible to separate these effects from that of the double layer distortion. Nevertheless, as pointed out by Heymann,<sup>9</sup> there are several indications that the relaxation often plays a part. In the first place the dielectric constant usually increases with the  $\zeta$ -potential (Fricke and Havestadt). Accordingly, it was found by Garreau and Marinesco<sup>10</sup> and also by Shutt<sup>11</sup> that the

<sup>6</sup> J. J. Bikerman, *J. Chim. Physique*, 1935, **32**, 285.

<sup>7</sup> A. Piekara, *Kolloid Z.*, 1932, **59**, 12.

<sup>8</sup> P. J. Denekamp and H. R. Kruyt, *ibid.*, 1937, **81**, 62.

<sup>9</sup> E. Heymann, *ibid.*, 1934, **66**, 229, 358.

<sup>10</sup> Garreau and Marinesco, *Compt. rend.*, 1929, **189**, 331.

<sup>11</sup> W. J. Shutt, *Trans. Faraday Soc.*, 1934, **30**, 893.

dielectric constant of albumins increases with increasing divergence from the iso-electric point. This is explained by a change in the dipole of the Zwitterion, but may partly be due to relaxation effects. Moreover, suspensions of spherical particles without dipolar character may also show a considerable increase in dielectric constant. Finally, it is mentioned by Heymann—although not as a support for the theory of relaxation—that the dielectric constant usually increases with the degree of dispersion. This is to be expected from (10): the smaller is  $R$ , the larger the difference between  $D$  and  $D'$  will be.

### Summary.

A survey is given of the theory of double layer distortion for charged spherical particles moving in an external electric field. An attempt is made to state explicitly all assumptions which underly the theory. The final formula for the cataphoretic velocity is mentioned and briefly discussed. It is further shown that the influence of the double layer distortion on the dielectric constant of the systems considered may account for certain properties found experimentally.

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## THE HELMHOLTZ.

BY E. A. GUGGENHEIM, M.A., Sc.D.

*Received 26th July, 1939.*

### 1. Preamble. Electric Dimensions.

I want to discuss the physical significance of the quantity commonly denoted by the symbol  $\zeta$ , and I hope to show that the habit of expressing  $\zeta$  in volts shows confusion of thought. In order to make my argument clear, it is expedient that I should first make a few remarks concerning the dimensions of electric quantities.

It is well known that in mechanics one has three independent dimensions. These are usually taken to be length, time, mass. There is, however, an infinite choice of other sets of three independent dimensions, and occasionally some other choice may be more convenient, for example, length, time, energy. It is obvious that the number of independent dimensions can, if desired, be artificially reduced by conventionally assigning the value unity to some universal dimensional constant. For example, if we conventionally take the velocity of light to be unity, then the dimensions, length, and time become indistinguishable according to this convention.

It is also well known that in thermodynamics there are four independent dimensions which we may conveniently take to be length, time, mass, temperature, or length, time, energy, temperature. Here, again, the number can be artificially reduced by convention. For example, if we assigned the value unity to the gas constant, the dimensions, energy and temperature would become merged into one.

In electrodynamics there are also four independent dimensions. This fact has been expounded with admirable lucidity by Sommerfeld,<sup>1</sup> but is skilfully obscured in the majority of text-books. As a matter of convenience, we may choose as the four fundamental dimensions, length, time, energy and charge. Obviously, there is an infinite variety of choice, and for many purposes, though not for the present purpose, it would be more convenient to choose mass rather than energy for the third fundamental dimension. Having made our choice of the fundamental dimensions, we can tabulate the dimensions of several derived electric quantities. We thus obtain:

<i>Quantity.</i>	<i>Dimensions.</i>	<i>Examples of unit.</i>
Dipole-moment	charge $\times$ length	faraday cm.
Superficial charge density	charge/length <sup>2</sup>	faraday/cm. <sup>2</sup>
Potential	energy/charge	joule/faraday
Field strength	energy/length charge	joule/cm. faraday
Current	charge/time	faraday/sec.

If we choose as units of length the centimetre, of time the second, of energy the joule, and of charge the faraday, then the units of the derived quantities are those given in the last column. I need hardly mention that I have deliberately chosen units familiar to everyone in the case of the fundamental quantities, but probably strange in the case of the derived quantities.

Let us now consider a plane with a uniform distribution of charge of superficial density  $\sigma$  and a parallel plane at a distance  $d$  with an equal but opposite charge density  $-\sigma$ . Such a charge distribution is, of course, a double layer, and the product  $\tau = \sigma d$  is called by Helmholtz<sup>2</sup> the moment of the double layer.

From the fundamental laws of electrostatics, that is to say by experiment, we know that the potential difference  $\phi$  across a double layer is proportional to the moment  $\tau$  of the double layer. We may therefore write

$$\phi = a\tau \quad \dots \dots \dots (1.1)$$

where  $a$  is a universal constant. This constant  $a$  is not a pure number, for its value depends on the units used. According to its definition  $\tau$  has the dimensions charge  $\times$  length/area, or charge/length, whereas  $\phi$  has the dimensions energy/charge. It follows that  $a$  has the dimensions energy length/charge.<sup>2</sup> In particular, if we use the units cm., sec., joule, faraday we have

$$a = 1.06 \times 10^{23} \text{ joule cm./faraday}^2 \quad \dots \dots (1.2)$$

Alternatively, we may use the C.G.S. units cm., sec., erg., but the value of  $a$  still depends on the unit of charge. Conversely, we can define the unit of charge by assigning a conventional value to  $a$ . In particular, the electrostatic unit of charge is defined by the convention

$$a = 4\pi \text{ erg. cm./}(\text{e.s.u. charge})^2 \quad \dots \dots (1.3)$$

In other words, in the electrostatic system of units the number of independent dimensions is artificially reduced from four to three by the convention of taking  $a/4\pi$  to be unity.

We shall see later that the commonly used electrokinetic formulæ contain a factor  $4\pi$  which is in reality the universal constant  $a$ ; this

<sup>1</sup> Sommerfeld, *Z. Technische Physik*, 1935, 11, 420.

<sup>2</sup> E.g., Helmholtz, *Ann. Physik*, 1879, 7, 338.

factor is therefore not a pure number but a quantity having the dimensions energy length/charge<sup>2</sup> and has the value  $4\pi$  erg. cm./ (e.s.u. charge)<sup>2</sup> if, and only if, these particular units are used.

## 2. Dielectric Constant.

What I have said so far about electric double layers is true for all double layers, thick or thin, as we have made no mention of how the double layer originates or to what it is attached. Let us now consider a simple example of a macroscopic (large scale) double layer, namely a parallel plate condenser. If the charge density on the plates is  $\pm \sigma$ , the distance between the plates is  $d$  and the space between the plates is empty, then the moment of the double layer is  $\tau = \sigma d$ , and the potential difference between the plates is  $a\tau = a\sigma d$ . If, however, the space between the plates is filled with a homogeneous isotropic dielectric, we must be careful to distinguish between the charge density  $\sigma_p$  on the positive plate and the resultant charge density  $\sigma_r$ , which is related to  $\sigma_p$  by the equation

$$\sigma_r = \sigma_p - \sigma_i \quad (2.1)$$

where  $-\sigma_i$  is the induced charge density on the dielectric at the end touching the positive plate. By the fundamental laws of electrostatics the electric potential difference  $\phi$  between the plates is given by

$$\phi = a\sigma_r d = a(\sigma_p - \sigma_i)d \quad (2.2)$$

Formula (2.2) can formally be rewritten as

$$\phi = aD\sigma_p d, \quad (2.3)$$

where the *dielectric coefficient*  $D$  is defined by

$$D = \frac{\sigma_r}{\sigma_p} = \frac{\sigma_p - \sigma_i}{\sigma_p} \quad (2.4)$$

The usefulness of this transformation depends on the fact that under normal experimental conditions  $D$  defined according to (2.4) is independent of  $\sigma_p$  (or of  $\phi$ ), and may then be called the *dielectric constant*.

All this is elementary, but, I think, not entirely superfluous if it serves to emphasise two important points.

(1) The dielectric coefficient  $D$  does not occur in the relation (2.2) between  $\phi$  and  $\sigma_r$ , but only in the relation (2.3) between  $\phi$  and  $\sigma_p$ . The dielectric coefficient is therefore irrelevant unless we wish to distinguish between the charge on the plates and the (induced) charges in the dielectric.

(2) The introduction of the *dielectric coefficient* is not particularly useful except when it is independent of the field strength; only in this case should it be called the *dielectric constant*.

## 3. History of Electrokinetic Formulæ.

The fundamental theory of the several electrokinetic phenomena is due to Helmholtz.<sup>3</sup> His derivation of formulæ is mathematically somewhat complicated because he gives this derivation in a form independent of the distribution of the ions forming the double layer. His final result can, however, as a matter of fact, be expressed in terms of the integrated moment across the whole double layer. If we are willing to accept on

<sup>3</sup> Helmholtz, *Ann. Physik*, 1879, 7, 337.



faith this independence of the details of the ionic distribution, then the whole derivation of Helmholtz's formulæ is tremendously simplified by replacing the actual diffuse double layer by an imaginary simple double layer of the same total moment. This simplified derivation is due to Perrin.<sup>4</sup> There is, however, a significant (or apparently significant) difference between the original formulæ of Helmholtz and the later formulæ of Perrin which I wish to discuss.

I have already mentioned that Helmholtz on the second page of his paper clearly defines the moment of the double layer, which I have denoted by  $\tau$ . He then says, in the next sentence, that this quantity is equal to the potential difference between the plates of a condenser divided by  $4\pi$ . From this statement it is patent:

(1) that Helmholtz was referring to the double layer composed of the actual or total resultant charge distribution, and was not attempting to decompose this distribution into a plate charge and an induced charge;

(2) that Helmholtz was using electrostatic units. The truth of (2) is further confirmed on page 352, where Helmholtz states explicitly that all quantities are measured in electrostatic units. Incidentally, in discussing experimental data Helmholtz gives the ratio of the potential differences under discussion to that of a Daniell cell. I think he never uses the word *volt*.

It is entirely unnecessary to refer to the formulæ for the several electrokinetic phenomena, as they are all mutually related. It will suffice if I recall the formulæ for electro-osmosis. For a liquid of viscosity  $\eta$  in a tube of radius  $r$  subjected to an electric field of strength  $X$  the flow  $f$  expressed as volume per unit time is given by

$$f = X \frac{\pi r^2}{\eta} \tau \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

where  $\tau$  is the moment of the double layer. We would emphasise that both sides of formula (3.1) have the dimensions length<sup>3</sup>/time, and the formula is therefore valid in any self-consistent set of units.

Helmholtz makes use of the substitution

$$\phi_i - \phi_a = 4\pi\tau \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

and regards  $\phi_i - \phi_a$  as the potential difference in electrostatic units across the double layer. If we substitute from (3.2) for  $\tau$  into (3.1), we recover (in altered notation) Helmholtz' original formula for electro-osmosis. Perrin, in a footnote, states that Helmholtz has forgotten to include the dielectric constant, and he uses instead of (3.2) the substitution

$$\zeta = 4\pi\tau/D \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

and regards  $\zeta$  as the potential difference across the double layer. Actually, Perrin used the symbol  $\epsilon$ , not  $\zeta$ . So far as I know, the use of the symbol  $\zeta$  is due to Freundlich,<sup>5</sup> whose definition of  $\zeta$  is precisely (3.3). I postpone further discussion of Helmholtz' formula (3.2) and Perrin's formula (3.3).

Before closing this historical summary, I must refer to Gouy's<sup>6</sup> well-known work. Again I do not propose to give any details, but only wish to recall that in the attempt to calculate the detailed configuration of

<sup>4</sup> Perrin, *J. Chim. Physique*, 1904, 2, 601.

<sup>5</sup> See Freundlich, *Colloid and Capillary Chemistry*, p. 242 (Methuen, 1926).

<sup>6</sup> Gouy, *J. Physique*, 1910, 9, 457.

the double layer Gouy treats the solvent as a continuous medium with a macroscopic dielectric constant. In other words, in his model the ions are analogous to the plates of a condenser and the solvent is analogous to a dielectric.

#### 4. Discussion of Classical Formulæ.

The question now arises which is the better formula (3.2) or (3.3) to substitute into (3.1). There seems to be almost unanimity in favour of Perrin's formula (3.3), but I think that this is unjustified. We saw in § 2 that the dielectric coefficient is a conception entirely irrelevant except when we want to distinguish specifically between the charge on a conductor and the induced charges in the dielectric. It therefore correctly enters into Gouy's attempt to calculate the ionic distribution because he specifically treats the solvent as a continuous dielectric. Since he ignores electric saturation in the neighbourhood of the ions, the dielectric coefficient is in his theory a constant. But until one becomes interested in the detailed configuration of the double layer the dielectric constant seems to me quite irrelevant, and I fail to see what is gained by substituting from (3.3) into (3.1).

Not only the formula for electro-osmosis, but all the formulæ for electrokinetic phenomena give direct information about the moment of the double layer, which we have denoted by  $\tau$ . As usually written, all these formulæ will be found to contain explicitly the factor  $D\zeta/4\pi$ , which is nothing else than  $\tau$ , the quantity which appears naturally in the simple derivation of the electrokinetic formulæ. I believe that many others besides myself will obtain a clearer and simpler picture of electrokinetic phenomena if they will drop the habit of translating the moment  $\tau$  of the double layer into an electric potential  $\zeta$  defined by (3.3) and then converted to volts by multiplication by 300.

#### 5. The Helmholtz as a Unit of $\tau$ .

If my suggestion is to be practical, it is expedient that we should have a convenient unit for  $\tau$ . The unit which seems particularly suitable is  $10^{-2}$  (e.s.u. charge)/cm. I would like to propose that this unit be called the **Helmholtz**. We then have

$$1 \text{ Helmholtz} = 1 \text{ Debye}/\text{\AA}^2 = 1 \text{ e.s.u. charge}/\text{m}.$$

The conversion of  $\zeta$  in volts to  $\tau$  in Helmholtz is then achieved by using

$$\zeta \text{ volts} = \frac{D}{12\pi} \tau \text{ Helmholtz},$$

or for water at ordinary temperature

$$\zeta \text{ volts} = 2.1 \tau \text{ Helmholtz}.$$

It is hardly necessary to mention that the same conversion factor will convert millivolts to milli-Helmholtz.

#### Summary.

1. The distinction between the moment  $\tau$  of an electrical double layer and the potential difference  $\phi$  across an electrical double layer is emphasised.
2. The measurement of the moment of an electrical double layer in volts shows confusion of thought.

3. It is suggested that a suitable unit of the moment of an electrical double layer is the **Helmholtz** defined as 1 Debye/A<sup>2</sup>.

4. The conversion factor from  $\zeta$  in volts to  $\tau$  in Helmholtz is

$$\zeta \text{ volts} = \frac{D}{12\pi} \tau \text{ Helmholtz.}$$

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## APPLICATION OF THE DEBYE-HÜCKEL THEORY TO DISPERSE SYSTEMS.

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It is well known that the components of disperse systems, whether particles or micelles, are electrically charged and move either to the anode or to the cathode in an electric field. Consider, for example, the solid phase of a disperse system, and the liquid phase in contact with it. The potential difference  $V$  between the two phases, as calculated by thermodynamics, is the potential difference between the boundary of the solid phase  $AA'$  (see Figure 1) and a point in the interior of the liquid remote from the phase boundary. But on account of the frictional forces which give rise to viscosity, there is a layer of liquid  $AA'B'B$  which adheres to the solid, and therefore in such phenomena as electroosmosis, streaming potentials and electrophoresis, it is necessary to consider the potential difference between this layer of liquid rigidly fixed to the particle and a point in the interior of the liquid. This potential difference is usually written  $\zeta$  and is called the electrokinetic potential. Numerous experimental comparisons, made chiefly by Haber and Klemesiewicz, Freundlich and Rona, Cameron and Ottinger, and Thon, have established the fact that the total potential difference  $V$  and the electrokinetic potential are entirely different.

### The Debye-Hückel Theory and the Electrokinetic Potential.

The potential gradient from the edge of the particle out into the solution may be obtained from the theory of Stern, but this theory contains a number of factors, such as chemical and adsorption potentials, about which insufficient is known to allow Stern's equations to be applied without ambiguity. Therefore several years ago it appeared preferable to the author<sup>1</sup> to treat this problem by making use of the approximation of considering only the properties of the ionic atmosphere surrounding the particle.\* Figure 1 shows that the potential gradient is divided into distinct regions. The first is that across the layer of liquid fixed rigidly to the particle, and is due to a complex and still incompletely determined mechanism, for in addition to the true Volta effect, which is

<sup>1</sup> R. Audubert, *C. R.*, 1932, **195**, 210, 306; *J. Chim. Physique*, 1932, **30**, 89; Harold and Abramson, *ibid.*, **15**, 575.

\* At the same time, but independently, Harold and Abramson applied the Debye-Hückel theory to the titration of proteins.

caused mainly by the dielectric orientation of polar molecules of the solvent, other charging processes will also occur either by adsorption or by electrochemical means.

The second part of the fall of potential is due essentially to an equilibrium between the electric forces acting on the ions and the thermal agitation. The calculation of the conditions of equilibrium of this diffuse layer near the phase boundary has been done by Chapman, and later by Gouy. The Debye-Hückel theory of strong electrolytes has enabled a more complete solution to be given for the potential gradient in the diffuse ionic atmosphere. If a central ion is considered according to this theory, the potential at a distance  $r$  is given by

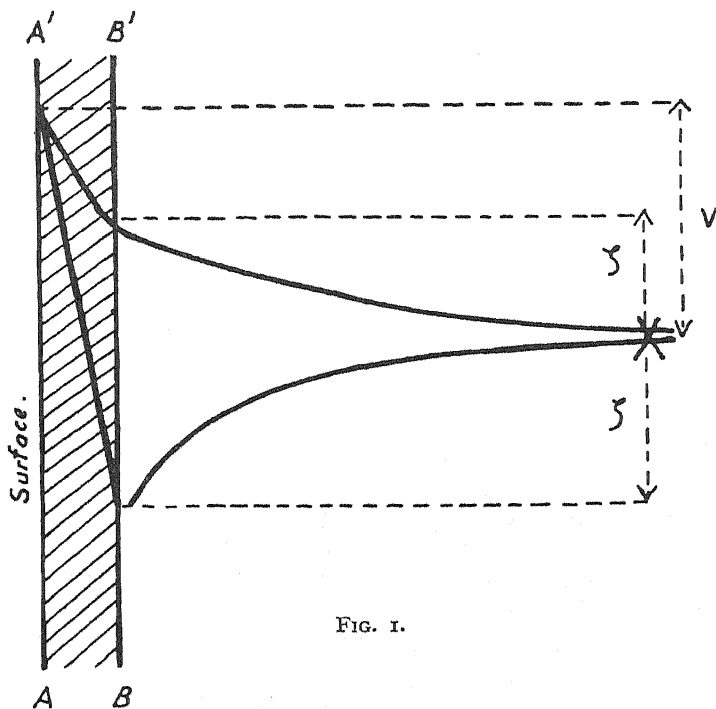


FIG. 1.

$\zeta = B \frac{e^{-\chi r}}{r}$ , where  $\chi$  is a quantity characteristic of the ionic atmosphere, and is equal to  $\sqrt{\frac{4\pi e^2}{DkT} \mu}$ ,  $e$  being the charge of an electron,  $k$  the Boltzmann constant,  $D$  the dielectric constant and  $\mu$  the ionic strength. Now consider a very dilute disperse system, the particles of which have a radius  $a$ , which is taken to mean the true radius plus the thickness of the liquid layer which adheres rigidly to the particle. The constant  $B$  is determined by the conditions at the surface of the particle, of which the charge is  $E$ , and the following equation is obtained:—

$$-\left(\frac{d\zeta}{dr}\right)_{r=a} = \frac{E}{a^2 D} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$B = \frac{E}{D} \cdot \frac{e\chi a}{1 + \chi a}.$$

The mobility  $u$  of the particle is a function of the electrokinetic potential and is given by  $u = \frac{D\zeta}{6\pi\eta}$ . If therefore the electrokinetic potential is identified with that of the ionic atmosphere, it follows that

$$u = \frac{E}{6\pi\eta a} \cdot \frac{1}{1 + aA\sqrt{\mu}}, \quad (2)$$

where  $\eta$  is the viscosity and  $A$  is a universal constant.

### Experimental Verification of the Theory.

Assuming for the case of spherical particles of the same kind that  $E$  is proportional to  $4\pi a^2$ , equation (2) can be transformed to

$$u = \frac{4}{6} \cdot \frac{\sigma}{\frac{1}{a} + A\sqrt{\mu}}, \quad (3)$$

where  $\sigma$  is the surface density of charge. If  $a$  is so big that  $1/a$  may be neglected in comparison to  $A\sqrt{\mu}$ , and if the charge is constant, the mobility of the particle becomes independent of its radius. This is precisely what has been observed in most cases.

Now consider the relative variation of the mobility,  $\frac{u_0 - u}{u_0}$ , where  $u_0$  is the mobility at infinite dilution, when  $\mu \rightarrow 0$ , and  $u$  is the mobility in a medium of ionic strength  $\mu$ . When  $\mu \rightarrow 0$ ,  $u = \frac{E}{6\pi\eta a}$ . Assuming for the time being that the charge  $E$  is not changed by addition of electrolyte, which will naturally only be true for very small additions, and which will be considered in more detail later, then

$$\frac{u_0 - u}{u_0} = \frac{aA\sqrt{\mu}}{1 + aA\sqrt{\mu}}, \quad (4)$$

and for very small particles this becomes

$$\frac{u_0 - u}{u_0} = aA\sqrt{\mu}. \quad (5)$$

For a given electrolyte the relative variation of the mobility is proportional to the square root of the ionic strength. As Quintin and the author showed,<sup>2</sup> this is observed experimentally for particles of various kinds, such as mastic, gamboge, charcoal, gold, silver and glass, in different media such as electrolytes and solutions of dyes. But it is interesting to examine the validity of equation (4) more exhaustively. Among the considerable number of determinations of mobilities met with in the literature, a large proportion do not appear sufficiently accurate for this purpose, many authors, for example, even neglecting the corrections for viscosity and the electroosmosis of the medium. Freundlich has published very good measurements on arsenic trisulphide and ferric hydroxide sols in many complex electrolytes, and the present author has also made a large number of measurements on spherical particles of gamboge and mastic in contact with solutions of strong electrolytes. The curves of figures 2, 3, 4 and 5 show the results of

<sup>2</sup> R. Audubert and M. Quintin, *J. Chim. Physique*, 1925, **23**, 176.

these experiments, and the conclusions to be drawn from them are as follows:—

For small concentrations all the curves have a part in common, corresponding to the region of validity of the theory. Then they diverge, the divergence being greater the greater the valency of the added ion of opposite sign to that of the charge of the particle. But if the ferric hydroxide sols only are considered, which have positively charged micelles, it is observed that two electrolytes whose active ions have the same valency, for example,  $[\text{Au}(\text{CN})_2]^- \text{K}^+$  and  $[\text{Au}(\text{CN})_4]^- \text{K}^+$ , or  $[\text{Cu}(\text{CN})_4]^- \text{K}_3^{+++}$  and  $[\text{Fe}(\text{CN})_6]^- \text{K}_3^{+++}$ , give different curves, so that in addition to changing the diffuse ionic atmosphere in the way

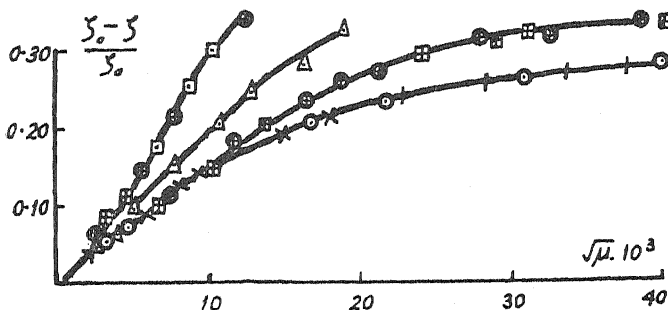


FIG. 2.\*—  
Gamboge.

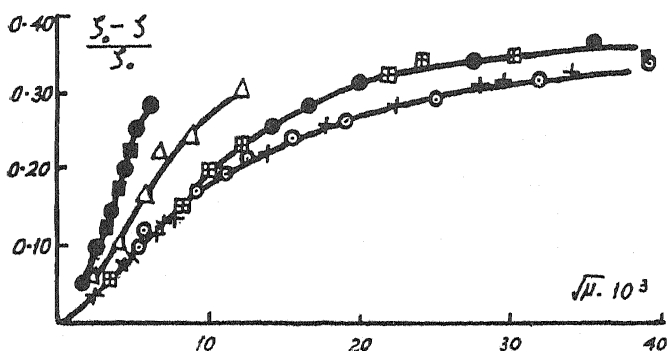


FIG. 3\*—  
Mastic.

\* Key to Figs. 2 and 3:  $\times$  KCl.  $\bigcirc$  NaCl.  $\otimes$  BaCl<sub>2</sub>.  $\boxplus$  MgCl<sub>2</sub>.  
 $\triangle$  H<sub>2</sub>SO<sub>4</sub>.  $\bullet$  (NO<sub>3</sub>)<sub>3</sub>La.  $\blacksquare$  Al(NO<sub>3</sub>)<sub>3</sub>.

described by the theory, these ions are causing specific effects. Acids and electrolytes which are hydrolysed to a large amount give curves which only verify the theory at the extreme limit of dilution, according to the results obtained with mastic and gamboge, and it will be seen later that such curves can be explained by a variation of the charge  $E$  with  $pH$ , which comes about because the particles of mastic and gamboge may be considered to be polymers of weak acids whose surface dissociation varies with the acidity of the liquid. For the sake of simplicity and for a first approximation the charge of the micelle has been considered to be constant, but it is well understood that it may vary owing to ionic adsorption, to chemical reactions of the surface or to electrolytic dissociation of the surface.

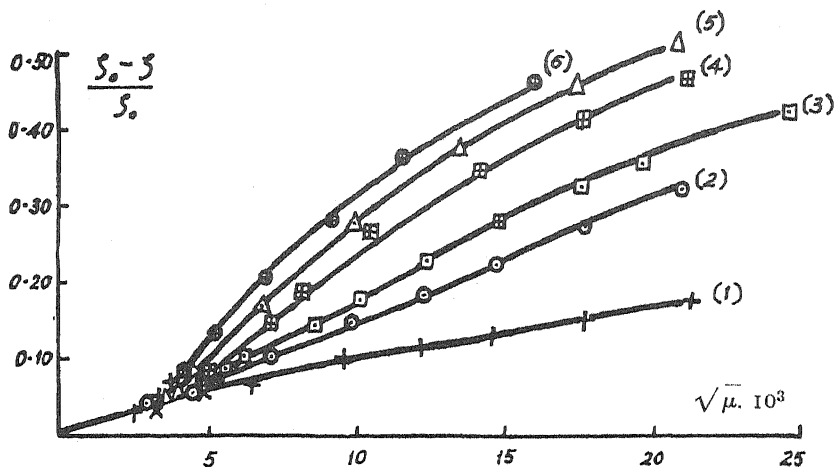


FIG. 4.—Ferric hydroxide.

- (1)  $[\text{Au}(\bar{\text{CN}})_2] \text{K}^+$ ; (2)  $[\text{Au}(\bar{\text{CN}})_4] \text{K}^+$ ; (3)  $[\text{Pt}(\bar{\text{CN}}_4)] \text{K}_2^{++}$ ;  
 (4)  $[\text{Cu}(\bar{\text{CN}}_4)] \text{K}_3^{+++}$ ; (5)  $[\text{Fe}(\bar{\text{CN}}_6)] \text{K}_3^{+++}$ ; (6)  $[\text{Fe}(\bar{\text{CN}}_6)] \text{K}_4^{++++}$ .

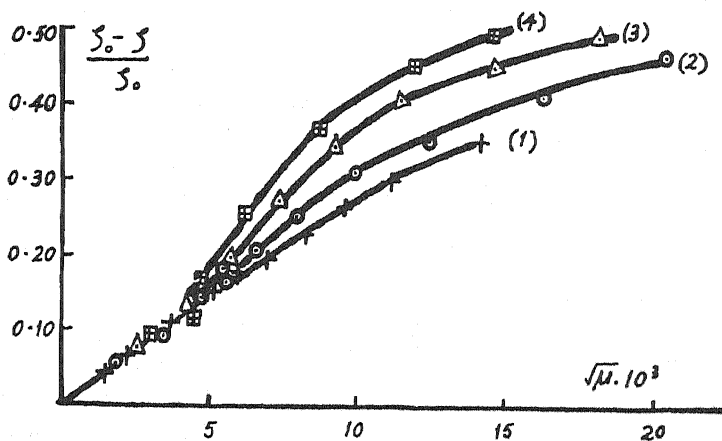


FIG. 5.—Arsenic trisulphide.

- (1)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)]\bar{\text{Cl}}$  and  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ ;  
 (2)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\bar{\text{Cl}}_2^-$ ; (3)  $[\text{Co}(\text{NH}_3)_6]\bar{\text{Cl}}_3^{--}$ ;  
 (4)  $[(\text{NH}_3)_4\text{Co} \begin{smallmatrix} \text{NH}_3 \\ \diagup \\ \text{OH} \end{smallmatrix} \text{Co}(\text{NH}_3)_4] \equiv \text{Co}_2(\text{NH}_3)_9\text{OH} \cdot 4\text{H}_2\text{O}$ .

### Determination of the Mean Radius of the Particles from the Theory.

It is easy to deduce the mean radius of the particles from the preceding results. It has been stated already that the coefficient of the approximate equation (5) gives the value of  $a$ , but it is more satisfactory

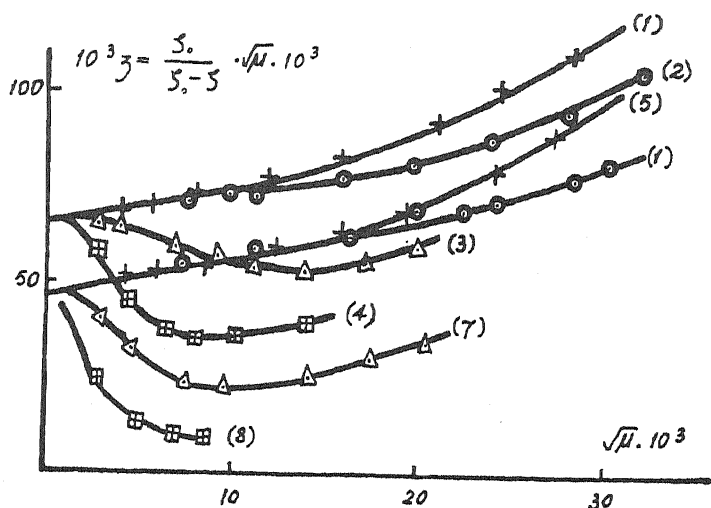


FIG. 6.

- |  |   |
|--|---|
| (1) Gamboge K <sup>+</sup> , Na <sup>+</sup> ; | (5) Mastic K <sup>+</sup> , Na <sup>+</sup> ; |
| (2) " Ba <sup>++</sup> , Mg <sup>++</sup> ;    | (6) " Ba <sup>++</sup> , Mg <sup>++</sup> ;   |
| (3) " SO <sub>4</sub> H <sub>2</sub> ;         | (7) " SO <sub>4</sub> H <sub>2</sub> ;        |
| (4) " La <sup>+++</sup> , Al <sup>+++</sup> ;  | (8) " La <sup>+++</sup> , Al <sup>+++</sup> ; |

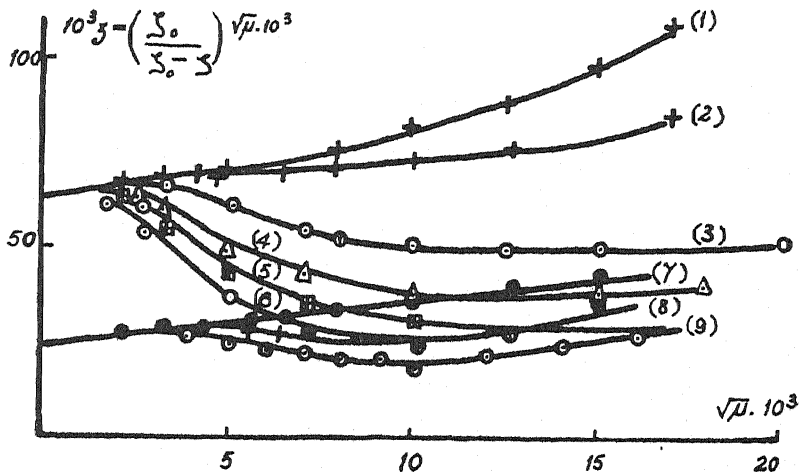


FIG. 7.

- |   |  |
|---|--|
| (1) Fe <sub>2</sub> O <sub>3</sub> , [Au(CN) <sub>2</sub> ] <sup>+</sup> K <sup>+</sup> ;   | (3) Fe <sub>2</sub> O <sub>3</sub> , [Pt(CN) <sub>4</sub> ] <sup>++</sup> K <sub>2</sub> ;                 |
| (2) " [Au(CN) <sub>4</sub> ] <sup>+</sup> K <sup>+</sup> ;  | (5) " [Fe(CN) <sub>6</sub> ] <sup>++++</sup> ;   |
| (4) " [Cu(CN) <sub>4</sub> ] <sup>+++</sup> K <sub>3</sub> ;  | (6) " [Fe(CN) <sub>5</sub> ] <sup>++++</sup> K <sub>4</sub> ;  |
| (7) As <sub>2</sub> S <sub>3</sub> , [Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup> and [Co(NH <sub>3</sub> ) <sub>4</sub> (CO <sub>2</sub> )] <sup>+</sup> Cl <sup>-</sup> · ½H <sub>2</sub> O. |  |
| (8) " [Co(NH <sub>3</sub> ) <sub>6</sub> Cl] <sup>+</sup> Cl <sub>2</sub> ;   | (9) As <sub>2</sub> S <sub>3</sub> , [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>+++</sup> Cl <sub>3</sub> . |



to obtain a value as follows: Writing  $z = \frac{u_0}{u_0 - u} \sqrt{\mu}$ , equation (4)

$$\text{becomes} \quad z = \frac{1}{aA} + \sqrt{\mu}. \quad (6)$$

If therefore  $z$  is plotted as a function of  $\sqrt{\mu}$ , the slope of the lines obtained should be equal to 1 by the theory, and  $a$  is obtained from the intercept at  $\sqrt{\mu} = 0$ , which equals  $1/aA$ . In this way, starting from the curves

TABLE I.

Mastic	$a = 0.8 \times 10^{-6}$ cm.
Gamboge	0.67
As <sub>2</sub> S <sub>3</sub>	1.43
Fe(OH) <sub>3</sub>	0.65

of figures 2, 3, 4 and 5, the bundles of curves of figures 6 and 7 were obtained, and apart from the case of acid solutions, they all have a common rectilinear portion which verifies equation (6). In all these cases this formula allows a value of

$a$  to be calculated, and for the different systems studied the results shown in Table I. were obtained.

### Determination of the Charge of the Particles from the Theory.

It may already be stated with certainty that the theory of Debye and Hückel is applicable to disperse systems in media of low ionic strength, and it will now be demonstrated that it allows the variation of the charge of the particles with the acidity of the liquid to be calculated, and also the surface dissociation constant of the substance, which ionization in certain cases gives rise to the charge at the phase boundary. Mastic sols were used for this work,<sup>3</sup> and the mastic is a resin and contains

4 % $\alpha$ and $\beta$ masticic acids	(Mol. Wt. 376.2)
0.5 % masticolic acid	(376.3)
38 % $\alpha$ and $\beta$ masticonic acids	(490.6)
30 % resins.	

All these are soluble in alcohol, and the remaining 27.5% is insoluble. The surface of the particles carries a negative charge, and it is easy to show that, at least for grains of small size, ( $< 1\mu$ ), this charge arises principally from superficial ionisation of acid groups in the periphery. Experimentally, using the necessary precautions, sols were titrated in twice distilled water, and the titre compared with that of the liquid from between the particles of the sol, obtained by ultrafiltration. Table II shows that for small grain sizes, the titratable quantity of soluble acids

TABLE II.

Number of Particles per c.c. of sol.	Radius of Particles (Calculated) (cm.).	OH Reacting with the Surface/Litre of Sol* (grams).	Per cent. OH Reacting with the Surface.	OH Reacting with 1 cm. <sup>2</sup> of Surface (grams).	OH Reacting with each Particle (grams).
$1.67 \times 10^{11}$	$0.18 \times 10^{-4}$	$1659 \times 10^{-5}$	81	$2370 \times 10^{-11}$	$950 \times 10^{-12}$
3.6	0.42	1566	84	1960	4300
$1.23 \times 10^{-9}$	1.25	113	43	470	9200
1.72	2.97	1	0.5	0.5	55

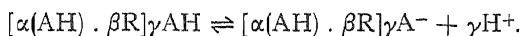
\* From the difference between the titre of the sol and of the ultrafiltrate.

<sup>3</sup> R. Audubert and Carpeni, *J. Chim. Physique*, 1938, 35, 115.

the filtrate is negligible compared with the total titratable quantity in the sol.

On the other hand, for sols with a large particle size, the results are altogether different, for the titratable surface acidity is small compared with the total titratable acidity in the ultrafiltrate. In these latter cases, therefore, the electrochemical phenomena are negligible, and the existence of the electric charge must be related to a contact mechanism of electrification, such as molecular orientation and the dielectric fixing of molecules of the solvent.

If the particles are considered to be spheres of such small diameter that the charge is due to surface ionisation the particle may be represented schematically as:  $[\alpha(\text{AH}) \cdot \beta\text{R}] \gamma\text{AH}$ , where R is the insoluble resin and AH the acid part. Following the notation of J. Duclaux, the symbols between the brackets represent the neutral portion of the micelle, and  $\gamma\text{AH}$  is the active part. Under these conditions the ionisation of the particle may be written:—



Or for conciseness, if S represents the inert part of the micelle which is attached to a molecule of acid AH, this becomes



The equilibrium constant  $K_a$  is therefore given by

$$K_a = \frac{[\text{SA}^-][\text{H}^+]}{[\text{SAH}]} \quad (7)$$

And writing concentrations instead of activities,

$$[\text{A}^-] = [\text{OH}^-]_{\text{fixed}} = \text{N}_{\text{OH}} - [\text{OH}^-]_{\text{free}}$$

and

$$[\text{AH}] = [\text{OH}^-]_{\text{max. fixed}} - [\text{OH}^-]_{\text{fixed}},$$

where N is the quantity of caustic soda required for the titration, and  $f$  the activity coefficient of the  $\text{OH}^-$ . Knowing  $\text{pH}$  therefore, it is easy to calculate  $K_a$ , and as an example of this, the results for mastic sols are given in Table III.

TABLE III.

	<i>ph.</i>	N Equivalents per litre.	$[\text{A}^-]$	$[\text{AH}]$	$K_a$	
Sol a	4.57	$3.53 \times 10^{-5}$	$3.53 \times 10^{-5}$	$6.43 \times 10^{-8}$	$0.15 \times 10^{-5}$	
	4.67	7.1	7.1	6.0	0.25	
	4.73	12	12	5.58	0.41	
	4.80	18	18	4.98	0.6	
	4.87	23.5	23.5	4.43	0.72	
	5.06	35.0	35.0	3.3	0.9	
	5.40	47	47	2.1	0.89	
	6.15	58.8	58.8	0.9	0.46	
						Mean $= 0.60 \times 10^{-5}$ Graphically $= 0.8 \times 10^{-5}$
Sol b	6.80	1.47	1.47	$11.26 \times 10^{-5}$	$0.21 \times 10^{-7}$	
	7.00	2.94	2.93	9.80	0.30	
	7.30	5.88	5.86	6.87	0.43	
	7.70	8.82	8.77	3.96	0.44	
	8.30	11.96	11.76	0.97	0.6	
						Mean $= 0.41 \times 10^{-7}$ Graphically $0.40 \times 10^{-7}$

But it is now possible to compare the experimental values of the mean dissociation constants with values calculated from the present application of the Debye-Hückel theory. It has been noted above that the relative variation of the electrophoretic mobility of particles of a suspension of mastic can only be calculated from the Debye-Hückel theory at the limit of small concentrations, and on account of the variation of  $p_H$  a divergence is observed between the theory and experiment. Let  $\Delta$  represent this deviation, then

$$\Delta = \left( \frac{u_n - u}{u_0} \right)_{\text{Expt.}} - \frac{aA\sqrt{\mu}}{1 + aA\sqrt{\mu}} \quad (8)$$

And if it is also assumed that this deviation is caused by a variation of the charge, and if  $E_0$  is the value of the charge before adding electrolyte and  $E$  its value at any given  $p_H$ ,

$$\frac{E_0 - E}{E_0} = \Delta(1 + aA\sqrt{\mu}) \quad (9)$$

Further by considering the equilibrium equation (7), and assuming that the essential structure of the spherical particle is not changed, *i.e.*, that

$$[S^-] + [SH] = \text{constant} = m_0 \quad (10)$$

equation (7) becomes

$$[S^-] = \frac{K_a m_0}{[H^+] + K_a} \quad (11)$$

For two values of  $p_H$  corresponding to  $[H^+]$  and  $[H^+]_0$  the ratio  $(E_0 - E)/E_0$  is given by

$$\frac{E_0 - E}{E_0} = \frac{[H^+] - [H^+]_0}{[H^+] + K_a} \quad (12)$$

which, in turn, gives

$$K_a = \frac{[H^+] - [H^+]_0}{\Delta(1 + aA\sqrt{\mu})} - [H^+] \quad (13)$$

when equation (9) is substituted in it. Equation (13) allows  $K_a$  to be calculated from the experimental results and the deviation of the experimental electrophoretic mobility curves from the theoretical curves obtained from the Debye-Hückel theory. The values of the constant  $K_a$  calculated from the theory are given in the third column of Table IV, and the values obtained from the mean of the electrometric titration curves are in the last column. These data show that for a certain range of  $p_H$ , although admittedly a narrow one, the experimental results agree satisfactorily with the calculated values. Harold and Abramson in their paper cited above,<sup>1</sup> found that the Debye-Hückel theory can be applied to the titration of proteins with a greater range of validity than that obtained here in the case of mastic. This difference is most probably due to the fact that proteins are true electrolytes for which the electrochemical factors play an essential part, while in the case of mastic sols other phenomena should be taken into account.

TABLE IV.

$[H^+]$	$A(1 + aA\sqrt{\mu})$	$K_a$	
$1.17 \times 10^{-6}$	$2 \times 10^{-2}$		$[H^+]_0 = 1.2 \times 10^{-6}$
2.65	7.8	$1.7 \times 10^{-5}$	$aA = 1 \times 10^3$
3.12	13.85	1.0	
8.0	38.2	0.98	$K_a \text{ (expt.)} = 1.8 \times 10^{-5}$
12.5	54.0	0.70	
20.0	58.0	1.3	
5	4.0	2.0	$[H^+]_0 = 4 \times 10^{-6}$
7	5.0	5.3	
8	10.0	3.5	$aA = 1.3 \times 10^3$
10	13.0	3.6	
11	15.0	3.5	$K_a \text{ (expt.)} = 3.8 \times 10^{-5}$
12	20.0	2.8	
14	25.0	2.6	
16	28.0	2.8	

### Conclusions.

It is clear that the theory of Debye and Hückel only applies to disperse systems in its classical form when the ionic strength of the solution is very small. This restriction, however, does not seem necessarily to be a fault of the theory itself, because it must be remembered that Debye and Hückel's equation has been integrated by using only the first term of a series, and it is probable that its limits of validity might be extended by using further terms of this series, as Gronwall and LaMer have done for the calculation of the activities of strong electrolytes. In addition, it must not be forgotten that in certain cases, as the present curves have shown, other surface processes such as selective adsorption and chemical reactions must be taken into consideration. But for all that, the application of the Debye-Hückel theory to disperse systems, even in its limited form, gives very important results, because it allows conclusions to be drawn about the processes by which the particle becomes charged, and allows the importance of the surface electrochemical phenomena to be estimated, as compared with selective adsorption and chemical reactions which may occur on the surface.

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# ELECTROKINETIC EQUATIONS AND SURFACE CONDUCTANCE. A SURVEY OF THE DIFFUSE DOUBLE LAYER THEORY OF COLLOIDAL SOLUTIONS.

By J. J. BIKERMAN.

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## 1.

If a spherical particle whose charge is  $e$  moves in an electric field  $X$ , the electric force on it is  $Xe$ . If the resistance of the surrounding liquid is due only to movement of the particle, this resistance is  $6\pi r\eta u$ ,  $r$  being the radius of the particle,  $u$  its velocity, and  $\eta$  the viscosity of the liquid. In steady state  $Xe = 6\pi r\eta u$ , or

$$u = \frac{Xe}{6\pi r\eta} \quad (1)$$

If, in calculating  $X$ , the disturbance of the field caused by the particle is neglected, then equation (1) may be termed the "zero order approximation." It has been more or less explicitly used<sup>1</sup> and gives results of a wrong order of magnitude.

Equation (1) is in error in two directions:

(a) As the liquid around the particle is also charged its movement in the electric field is no consequence of the movement of the particle; therefore the resistance encountered by the particle is not  $6\pi r\eta u$ .

(b) The field strength is affected by the shape, size, and electric properties of the particle and by the charges on the particle and around it. The value of  $X$  varies at various points in the neighbourhood of the particle and is different from the value  $V/l$  calculated from the potential difference  $V$  and the mutual distance  $l$  of the electrodes.

Mathematical difficulties have prevented the derivation of an equation for spherical particles which would take into account all the corrections listed in the preceding paragraph. Smoluchowski,<sup>2</sup> after writing down the equations for the motion of a sphere, introduced three simplifications which reduced his equations to those valid for plane surfaces;<sup>3</sup> accordingly his final expression for  $u$  agreed with that of Helmholtz. A much more thorough investigation of the motion of spherical particles was published by Henry,<sup>4</sup> but he had to assume that the conductivity of the surrounding liquid was independent of the distance from the particle. Although it is unlikely that the abandonment of this inexact assumption would cause any essential change of the theory, it would be worth while examining the extent of the error due to it.

In order to simplify the calculations both Smoluchowski and Henry assumed a simple overlapping of the potentials due to the external

<sup>1</sup> J. W. McBain and Williams, *Colloid Symp. Monog.*, 1930, 7, 105.

<sup>2</sup> M. Smoluchowski, *Bull. Acad. Cracovie, math.-nat.*, 1903, 182.

<sup>3</sup> H. Helmholtz, *Ann. Physik*, (3), 1879, 7, 337.

<sup>4</sup> D. C. Henry, *Proc. Roy. Soc., A*, 1931, 133, 130.

charges and of those produced by the colloid particle and its "diffuse double layer." Komagata<sup>5</sup> and Hermans<sup>6</sup> repeated Henry's derivation without taking the overlapping for granted, but many other approximations which were necessary in view of mathematical difficulties impaired the validity of their results.

## 2.

More progress has been achieved in calculating the motion of rod or plate-shaped particles oriented in the direction of the current. If the rods are so long that the conditions at their advancing and receding edges may be neglected, then the lines of the liquid flow and of the electric current are straight lines and their mathematical treatment becomes relatively simple.

For this case the equation of Helmholtz<sup>3</sup>

$$u = \frac{D\zeta X}{4\pi\eta} \quad (2)$$

holds;  $D$  is the dielectric constant of the liquid and  $\zeta$  the potential difference between the liquid layer adjacent to, and moving with, the particle and the liquid far from the particle.  $X$  is the field strength parallel to the particle liquid interface. Contrary to what happens with spherical particles it is independent of the distance from this interface, but—even for rods or plates—it cannot be set

$$X = V/l. \quad (3)$$

The calculation of the value of  $X$  is most conveniently done when the notion of the surface conductance is introduced. In order to make the principle of the calculation as clear as possible let us consider a system which may not be easy to realise. It is an H-shaped tube\* (like a normal element), and its horizontal part is drawn in Fig. 1. A and B are perforated electrodes (e.g., of AgCl). Black lines signify interfaces having  $\zeta = 0$ , and thin lines those having a high  $\zeta$  value.

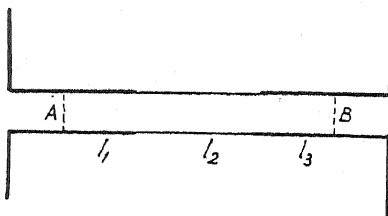


FIG. 1.

After the H tube has been filled with a solution of a binary electrolyte (e.g.,  $\text{AgNO}_3$ ) and an adsorption and solubility equilibrium has been reached, the equality  $[\text{Ag}^+] = [\text{NO}_3^-]$  is satisfied everywhere except near the wall of the capillary  $l_2$ . Therefore the solution in this capillary has a conductance differing from that of the solutions filling the capillaries  $l_1$  and  $l_3$ . If the circumference of the capillary is  $\Omega$ , its cross-section is  $S$ , the surface conductivity in the middle capillary is  $\chi \text{ ohm}^{-1}$ , and the specific conductivity of the solution far from the walls is  $\kappa \text{ ohm}^{-1} \text{ cm}^{-1}$ , then the total specific conductivity of the liquid in the middle capillary is  $\kappa + \chi \frac{\Omega}{S}$ . When a potential difference  $V$  is established between the electrodes A and B, the current strength in the steady state

<sup>5</sup> S. Komagata, *Res. Electrotechn. Lab. Tokyo*, 1935, No. 387.

<sup>6</sup> J. J. Hermans, *Phil. Mag.*, 1938, (7), 26, 650.

\* Some provision may be made to avoid a pressure difference between both compartments.

is constant over the whole distance AB. Accordingly

$$S\kappa X_1 = S\kappa X_3 = S\left(\kappa + \chi \frac{\Omega}{S}\right) X_2, \quad (4)$$

$X_1$  etc. being the field intensities in the corresponding parts of the capillary. Hence the field strength ( $X_2$ ) causing the motion of the liquid, *i.e.*, the field strength to be inserted into equation (2) is

$$X_2 = X_1 \frac{\kappa S}{\kappa S + \chi \Omega} = \frac{V}{l_2 + (l_1 + l_3) \frac{\kappa S + \chi \Omega}{\kappa S}} \quad (5)$$

When applied to usual forms of apparatus equation (5) needs an extension as the cross-sectional areas  $S$  are generally different along  $l_1$ ,  $l_2$ , and  $l_3$ . But even in its simplest form it shows the influence of the surface conductance on the effective field intensity.

As  $\chi$  is almost always positive<sup>7</sup> the sum  $l_2 + (l_1 + l_3) \frac{\kappa S + \chi \Omega}{\kappa S}$  is nearly always larger than  $l = l_1 + l_2 + l_3$ . Consequently  $X_2$  is less than the field strength calculated from equation (3).<sup>8</sup> As the measurable velocity  $u$  is proportional to the product  $X\zeta$  a too high value of  $X$  gives values of  $\zeta$  which are too low; the true  $\zeta$  values in dilute solutions often reach 0.15 volts and even more.

The difference between the uncorrected and the true field strength increases with the (dimensionless) ratio  $\chi\Omega/\kappa S$ . The error involved in employing equation (3) is therefore the larger the finer is the capillary (or the finer are the pores of the membranes) and can cause a variation of the apparent potential ( $\zeta'$ ) with the pore size when the true potential  $\zeta$  remains constant. A decrease of  $\zeta'$  in very narrow pores was observed by many workers, for instance by Manegold and Solf<sup>9</sup> for electro-osmosis, and Bull and Gortner<sup>10</sup> for streaming potentials.

At a constant  $\zeta$  potential the surface conductivity  $\chi$  is nearly proportional to the square root of the ionic concentration ( $C^{\frac{1}{2}}$ ) whilst  $\kappa$  in dilute solutions is nearly proportional to the concentration  $C$  itself. Thus,

$$\frac{\chi}{\kappa} = \text{const. } C^{-\frac{1}{2}} \quad (6)$$

This means that in a given apparatus (*i.e.*, at a constant ratio  $\Omega : S$ ) the true field diminishes when the dilution increases. At very high dilutions the field and therefore the observed electro-osmotic mobility are small whatever the value of  $\zeta$  may be. In the usual case of  $\zeta$  values increasing with dilution this causes a maximum of the electro-osmotic mobility and the streaming potentials.<sup>11, 12</sup> It was formerly believed that this maximum indicated a maximum value of  $\zeta$  or even of the charge  $e$ , and efforts have been made to explain this "discharge" at high dilutions. Recently Rutgers, Verlende, and Moorkens<sup>13</sup> have successfully tested the interpretation of the maximum of  $\zeta'$  given above; they compared the streaming potentials in capillaries of different bores.

<sup>7</sup> J. J. Bikerman, *Z. physik. Chem.*, A, 1933, **163**, 378.

<sup>8</sup> J. J. Bikerman, *J. physik. Chem.*, 1935, **39**, 243.

<sup>9</sup> E. Manegold and Solf, *Kolloid-Z.*, 1931, **55**, 293.

<sup>10</sup> H. B. Bull and Gortner, *J. physik. Chem.*, 1932, **36**, III.

<sup>11</sup> J. J. Bikerman, *Z. physik. Chem.*, A, 1934, **171**, 209.

<sup>12</sup> J. J. Bikerman, *Kolloid-Z.*, 1935, **72**, 100.

<sup>13</sup> A. J. Rutgers, Verlende and Moorkens, *Proc. Ned. Akad. van Wetensch.*, 1938, **41**, 763; 1939, **42**, 71.

The case of a rod-shaped particle oriented in the direction of the current is so similar to that of a capillary that the arguments of the preceding paragraphs may be immediately applied here. There are, of course, two important differences between the cases. (a) The length  $L$  of the particle (corresponding to  $l_2$  above) is small compared with the distance between the electrodes  $l$ . (b) The charges brought to the opposite ends of the rod by the surface current are dissipated through the whole volume of the solution. Taking into account the points (a) and (b) equation (5) becomes (for rods having half-spherical ends)

$$X = \frac{V}{l} \cdot \frac{\kappa(L-r)}{\kappa(L-r) + 2\chi} \quad (7)$$

and the true electro-kinetic potential <sup>11</sup> ( $r$  is the radius of the cylindrical rod)

$$\zeta = \zeta' \frac{\kappa(L-r) + 2\chi}{\kappa(L-r)} \quad (8)$$

It is seen that also here  $\zeta > \zeta'$  and that the difference  $\zeta - \zeta'$  increases with dilution and can cause a maximum of  $\zeta'$ . As equations (7) and (8) are only valid for particles which are large compared with the "thickness of the equivalent double layer" they do not give any information about the relation between  $\zeta$  and  $\zeta'$  when the particle size decreases and approaches molecular dimensions.

It may be worth while to show how large can be the difference between  $\zeta'$  and  $\zeta$ . In the system glass/0.0005 N. KCl  $\chi$  appears to be  $2 \cdot 10^{-9}$  ohm<sup>-1</sup>. As the specific conductivity of 0.0005 N. KCl is  $7.5 \cdot 10^{-5}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, the ratio  $\zeta : \zeta'$  for thin rods  $2 \cdot 10^{-4}$  cm. long is 19 : 15. In more dilute solutions this ratio may be as high as 2 or more.

It attains very high values if the solution contains exceptionally small numbers of ions, for instance in carefully dialysed aqueous sols or in purified organic liquids.<sup>14</sup> Such systems show almost no electro-osmotic or cataphoretic movement at all although their  $\zeta$  potential may have a usual value. In cases of dialysed SiO<sub>2</sub> sols<sup>15</sup> which are nearly immobile in an electric field the presence of a sufficient  $\zeta$  potential is made probable by their relative stability.

### 3.

Calculation of  $\zeta$  from (8) or from the complete formula

$$\zeta = \frac{4\pi\eta l}{DV} \cdot \frac{\kappa(L-r) + 2\chi}{\kappa(L-r)} \cdot u, \quad (9)$$

or in other words consideration of the surface conductance alters also the values previously obtained for the charge on a colloidal particle.<sup>16, 17</sup> According to Gouy's theory of the diffuse double layer the charge density  $\sigma$  for high  $\zeta$  values is approximately

$$\sigma = KC^{\frac{1}{2}}e^{k\zeta},$$

$K$  and  $k$  being constants. The term  $C^{\frac{1}{2}}$  tends to lower  $\sigma$  with increasing dilution; since Abramson used the apparent potentials  $\zeta'$  which also, after passing through a maximum, decrease with diminishing  $C$ , he

<sup>14</sup> F. Fairbrother and Malkin, *J. Chem. Soc.*, 1931, 1564.

<sup>15</sup> A. I. Baibaev and Kargin, *Acta physicochimica*, 1935, 3, 97.

<sup>16</sup> H. A. Abramson, *J. physico. Chem.*, 1935, 39, 749.

<sup>17</sup> L. S. Moyer and Bull, *J. gen. Physiol.*, 1935, 19, 239.



obtained a rapid fall of the surface density at large dilutions. This fall appears strongly reduced if equation (9) is used; sometimes  $\sigma$  seems to be nearly constant down to very small concentrations. Unfortunately these calculations apply only to capillaries, membranes, and coarse sols since in fine sols not only the equation (9) but also the value of the surface conductivity become uncertain. If more extensive experiments should confirm the constancy of  $\sigma$  within a reasonable range of ionic concentrations the theory of colloidal phenomena will be much simplified.

The earlier theory ascribed every change of the cataphoretic mobility to a change of the electric density  $\sigma$ , *i.e.*, to adsorption or desorption of ions. (Another expression for the same phenomenon was "a change of the electrolytic dissociation of the micelle.") When an electrolytic and a colloidal solution are mixed the specific conductivity of the mixture is not equal to the mean of the conductivities before mixing. This effect was considered to be an independent proof of an adsorption (or desorption). But the theory of the diffuse double layer shows that noticeable alterations of the conductivity are possible without any sorption of ions. What is called intermicellar liquid is no uniform solution; it consists of an almost infinite number of "shells" grouped around each colloidal particle; and each of these "shells" has its own ionic concentration and, when subject to an electric field, its own mobility. An addition of new ions to such a system causes their re-distribution among the shells and therefore an alteration of the conductivity.

But the conductivity, *i.e.*, the sum of the individual ionic mobilities, is less sensitive to re-distribution of ions than the mobilities themselves. If to an  $\text{As}_2\text{S}_3$  sol,  $\text{NH}_4\text{Cl}$  is added, the mobility of the  $\text{NH}_4$  ion is strongly reduced and the magnitude of this reduction agrees with that calculated on the assumption that  $\text{NH}_4$  ions without being adsorbed are present in the neighbourhood of the  $\text{As}_2\text{S}_3$  particles and are carried along by the water stream produced by the motion of the colloid spheres.<sup>18</sup>

An analogous alteration of mobilities takes place, of course, also in capillaries or membranes. It is generally believed to be one of the causes determining the transference numbers in membranes.

If a membrane be subject to an alternating field the surface conductance in its pores may also determine its polarisation capacity.<sup>12</sup> In electrostatics it is demonstrated that a boundary separating two regions having the field intensities  $X_1$  and  $X_2$  (both are, of course, normal to the boundary, and the dielectric constant is identical on both sides of it) is charged, and the amount of charge per square centimetre is

$$-\frac{D}{4\pi}(X_1 - X_2)$$

or, introducing equation (5),

$$-\frac{D}{4\pi}X_1 \frac{\chi\Omega}{\kappa S + \chi\Omega} \quad . \quad . \quad . \quad (10)$$

In an alternating field of frequency  $\omega$  this charge (and an equal charge of the opposite sign at the frontier between  $l_2$  and  $l_3$ , see Fig. 1) has to

<sup>18</sup> J. J. Bikerman, *Trans. Faraday Soc.*, 1937, **33**, 560.

\* At very high frequencies the surface conductance may be lower than in a constant electric field but for the usual range of frequencies the difference may be neglected. See Rosenhead and Miller<sup>19</sup> and also White<sup>20</sup>.

<sup>19</sup> L. Rosenhead and Miller, *Proc. Roy. Soc., A*, 1937, **163**, 298.

<sup>20</sup> P. White, *Phil. Mag.*, 1938, (7), **26**, 49.

be re-formed  $2\omega$  times per sec. In liquids containing but little ions ( $\kappa < 10^{-6}$  ohm $^{-1}$  cm. $^{-1}$ ) and at high frequencies ( $\omega > 10^4$  sec. $^{-1}$ ) the current spent for this polarisation easily becomes equal to or even greater than the ordinary Ohmic current. Although the polarisation of porous materials has several times been measured its evaluation from the point of view of surface conductance has only just started.<sup>21</sup>

If an alternating field be applied to a colloidal solution the colloid particles also are polarised and become induced dipoles. The dielectric constant of the sol increases in comparison with that of the intermicellar liquid (1) because of that polarisation and (2) because the induced dipoles are oriented by the electric field. The second term has not yet been computed satisfactorily but for the limiting case of high field intensities and low frequencies it can be shown<sup>22</sup> that the difference between the dielectric constant  $D_0$  of a sol containing rod-shaped particles and the dielectric constant  $D$  of the medium is given by the equation

$$D_0 - D = D \frac{cL}{r} \cdot \frac{2\chi}{\kappa(L-r) + 2\chi}; \quad (11)$$

$c$  is the volume concentration of the colloid (it is a pure number); all the other symbols have already been used in equations (7) to (9). Calculations of dipole properties based on this theory seem to give a satisfactory interpretation not only of the dielectric constant of sols but also of the Kerr effect in them.<sup>23</sup>

#### 4.

It is well known that the fundamental equation of electrokinetics (see equation 2)

$$\zeta = \frac{4\pi\eta}{DX}u \quad (12)$$

although extensively employed has never been tested. It is possible to measure all the magnitudes present in the right-hand term but the equation cannot be checked as long as there exists no independent method of determining  $\zeta$ . A comparison of two or many of the four basic electrokinetic effects (*i.e.*, electro-osmosis, cataphoresis, streaming and sedimentation potentials) on one system does not help since  $\zeta$  always cancels. These phenomena can therefore be accounted for by using any value of  $\zeta$ . The position changes completely when the surface conductance is considered. The following example shows that then the value of  $\zeta$  becomes unambiguous.

Suppose that the observed velocity  $u$  gives  $\zeta = 0.1$  volt if  $D$  is set equal to 80. Helmholtz did not introduce  $D$  in his equations; also in more recent time it was intimated that  $D$  within the double layer might have the value 1. This assumption would increase the value of  $\zeta$  from 0.1 to 8 volts without in any way disturbing the agreement between the experimental magnitudes of the four basic effects. But an increase of  $\zeta$  from 0.1 to 8 volts—although  $D\zeta$  remains constant—would shift the order of magnitude of surface conductivity from  $10^{-9}$  ohm $^{-1}$  to  $10^{57}$  ohm $^{-1}$ !

<sup>21</sup> H. Fricke and Curtis, *J. physic. Chem.*, 1937, **41**, 729.

<sup>22</sup> J. J. Bikerman, *J. Chimie Physique*, 1935, **32**, 285.

<sup>23</sup> J. Errera, Overbeek and Sack, *ibid.*, **32**, 681.

The high sensitivity of the calculated surface conductivity to small changes of the  $\zeta$  potential is due to the fact that the expression for  $\chi$  at high  $\zeta$  values consists of two terms which are approximately proportional to the products  $D^{1/2}e^{k\zeta}$  and  $D^{3/2}e^{k\zeta}$ . An 80-fold decrease of  $D$  lowers the numbers  $D^{1/2}$  and  $D^{3/2}$  but the increase of  $e^{k\zeta}$  on an 80-fold increase of  $\zeta$  is, of course, very much more important.

When the surface conductance is taken into account the four basic electrokinetic effects also become sensitive towards the true value of the potential. Let us consider for instance, equation (9). As long as  $\zeta$  and  $\chi$  are small the factor  $\frac{\kappa(L-r) + 2\chi}{\kappa(L-r)}$  is not far from unity, and the observed velocity  $u$  does not much depend on the dimensions of the particles (*i.e.*, on  $L$  and  $r$ ). But if  $\zeta$  had a value of several volts the correction factor would be nearly equal to  $\frac{2\chi}{\kappa(L-r)}$  and the velocity would be proportional to  $L-r$ . This consequence is in contradiction with experimental facts.

## 5.

The theories of electro-osmotic and cataphoretic mobilities on one hand and of ionic mobilities on the other hand started so differently that no physical relation between both sets of phenomena was apparent. The theory of electrokinetics postulated that :

- (i) the liquid moved as a whole relative to the solid (wall or particles) ;
- (ii) electrostatic forces were operating between the positive and negative charges in the double layer, and
- (iii) the nature of the charges was irrelevant.

The theory of electrolytes based on the assumptions that :

- (i) only ions moved and the liquid was unconcerned ;
- (ii) the ions were completely independent of each other, and
- (iii) there was no charge except those carried by ions.

After the electrokinetic theory admitted that only ions formed the double layer, and the ionic theory took note of the movement of the liquid around, and the electrostatic forces between, the ions no essential difference between the theories remains.

## Summary.

Consideration of the surface conductance of capillary and colloidal systems necessitates an alteration of most electrokinetic equations. The corrected equations account for many well-known observations like the maximum of the electrokinetic potential  $\zeta$ , the high dielectric constant of some sols, and so on. In variance with the uncorrected the new equations can be checked and give definite values of  $\zeta$ .

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## PART II.—(B) ABSORPTION POTENTIALS.

### ADSORPTION POTENTIALS. PART I.—GENERAL THEORY.

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Changes in the electrical potential difference across a system that arise from the formation of an adsorbed layer between two of its phases are of interest, since data about such potential differences have assisted the interpretation of the structure of monolayers and multilayers, and also because they affect electrocapillary curves. Potentials arising from a diffuse adsorption layer, from a continuous monolayer or from micromembranes consisting of multilayers may all be discussed under the heading of adsorption potentials. Bioelectrical potentials seem to arise at the surface of living cells, and these surfaces have electrical capacities that indicate that they are not more than a few molecules thick<sup>1</sup> if polarisation capacities can be interpreted in terms of a parallel plate condenser model. Some biophysicists considering the cell surface to be a thin oil phase have studied oil-water potentials. Beutner<sup>2</sup> considered these potentials to be located at the interfaces. Cremer<sup>3</sup> thought they might be explained as diffusion potentials, while Bauer<sup>4</sup> at one time and recently Ehrensvärd and Sillén<sup>5</sup> considered them to be adsorption potentials.

#### The Theory for the Bulk Phases Initially in Equilibrium

The potential difference between two bulk phases in equilibrium cannot permanently be altered by the adsorption at a plane interface, at given temperature and pressure, of a layer, that is insoluble in both bulk phases and is permeable to at least one ionic species, provided that the layer is sufficiently small compared to each of the bulk phases.<sup>6</sup>

Let the interface be permeable to ions of species  $i$  whose electrochemical and chemical potentials in phases I and II are denoted respectively by  ${}^I\bar{\mu}_i$ ,  ${}^I\mu_i$ ,  ${}^{II}\bar{\mu}_i$ , and  ${}^{II}\mu_i$ . Let the electrical potential of

<sup>1</sup> See, for example, Gray, *Experimental Cytology* (Cambridge, 1931), pp. 359-362. Fricke and Morse, *J. Gen. Physiol.*, 1925, 9, 137, 153. Cole, *ibid.*, 1928, 12, 37; 1936, 19, 609, 625; *Trans. Faraday Soc.*, 1937, 33, 966.

<sup>2</sup> Beutner, *Physical Chemistry of Living Tissues and Life Processes* (Baillière, Tindal and Cox, 1933).

<sup>3</sup> Cremer, *Z. f. Biol.*, 1906, 47, 1.

<sup>4</sup> Baur and others, *Z. Elektrochem.*, 1913, 19, 590; 1918, 24, 100; 1919, 25, 151; 1922, 28, 421; 1925, 31, 514; 1926, 32, 547; and *Z. physik. Chem.*, 1916, 92, 81; 1922, 103, 39; 1923, 106, 157.

<sup>5</sup> Ehrensvärd and Sillén, *Nature*, 1938, 141, 789.

<sup>6</sup> Craxford, Gatty and Rothschild, *Nature*, 1938, 141, 1098. Gatty and Spooner, *The Electrode Potential Behaviour of Corroding Metals* (Oxford, 1938). Gatty, *Trans. Faraday Soc.*, 1937, 33, 1087.

phases I and II against earth be denoted respectively by  ${}^I\psi$  and  ${}^{II}\psi$ . Then since  ${}^I\bar{\mu}_i = {}^I\mu_i + z_i F \psi$ , etc., where  $z_i$  denotes the valency of ion  $i$  having respect for sign and  $F$  is the Faraday, it is possible putting

$$\begin{aligned} \Delta\bar{\mu}_i &\text{ for } ({}^{II}\mu_i - {}^I\mu_i), \text{ etc., to write} \\ \Delta\bar{\mu}_i &= \Delta\mu_i + z_i F \Delta\psi \end{aligned} \quad (1)$$

and for two phases initially in equilibrium it is known that  $\Delta\bar{\mu}_i = 0$ . Writing  $\Delta\Delta\bar{\mu}_i$  for the increment in  $\Delta\bar{\mu}_i$  after the formation of an adsorbed layer, etc., (1) becomes

$$\Delta\Delta\bar{\mu}_i = \Delta\Delta\mu_i + z_i F \Delta\Delta\psi. \quad (2)$$

If  $\Delta\Delta\bar{\mu}_i^*$  refers to a time when equilibrium has been allowed to re-establish itself,  $\Delta\Delta\bar{\mu}_i^* = 0$ , since  $\Delta\bar{\mu}_i = 0$  both before and after the adsorption.

If the interphase is small in bulk compared to both of the bulk phases the formation at constant temperature and pressure of an adsorbed layer of a substance insoluble in both bulk phases cannot appreciably affect the concentrations of any component in either bulk phase, provided that the interphase is plane so that changes in surface tension cannot affect the condition of equality of pressure for the two phases. Under the above conditions the temperature, pressure, and composition of each bulk phase remains unaltered and therefore  $\Delta\Delta\mu_i^* = 0$ . It follows therefore from (2) and the value for  $\Delta\Delta\bar{\mu}_i^*$  that  $\Delta\Delta\psi^* = 0$ . If  $\Delta\psi$  is measured by means of reference electrodes of the type of saturated calomel half cells the observed potential against earth can be denoted by  $({}^I\psi + {}^IL)$ , etc., where  ${}^IL$  denotes a liquid-liquid junction potential plus a constant. The reasons for writing  $\Delta\Delta\mu_i^* = 0$  are sufficient to prove that  $\Delta\Delta L^* = 0$ . Thus

$$\left. \begin{aligned} \Delta\Delta\psi^* &= 0 \\ \Delta\Delta(\psi + L)^* &= 0 \end{aligned} \right\} \quad (3)$$

Addition of a soluble adsorbate to a system in general leads to non-zero values for  $\Delta\Delta\psi$  in the equilibrium case and  $\Delta\Delta\psi$  is located in the interphase if the two phases are electrically conducting phases; nevertheless the value for  $\Delta\Delta\psi^*$  depends on the dissolution of the substance in the bulk phases rather than on its adsorption at the interface.

Spreading a monolayer of oriented dipoles produces an electrical potential difference between two phases owing to the dipole field, which latter would not extend beyond the dipoles if the latter could be "smoothed" so as to behave like a parallel plate condenser and if short range forces could be neglected. The process of spreading also has the mechanical effect of sweeping away the double layer between the phases owing to viscous forces.<sup>7</sup> Thus  $\Delta\Delta\psi$  initially has a non-zero value which subsequently falls to zero.

The electrical polarisation of an interface in general produces a back electromotive force due to the charging of the capacity of the interface, and another due to concentration polarisation which affects the potential directly and also indirectly, since it affects the resistance and so the potential while current flows. The former polarisation decays with a time constant equal to the appropriate capacity resistance product and the latter by a diffusion process. The latter time constant will depend on the intensity of the polarising current and on its

<sup>7</sup> Schulman and Teorell, *Trans. Far. Soc.*, 1938, **34**, 1337.

duration, while the former might be expected to be independent of both these factors for low current densities.

### The Theory of Phases Initially in Partition Disequilibrium.

When  $\Delta\psi$  is a diffusion potential  $\Delta\Delta\psi$  need not be zero when a state of steady diffusion is reached. Thus spreading an insoluble monolayer between two phases in partition disequilibrium should lead to an initial surge in potential followed by a change in  $\Delta\Delta\psi$  to a value corresponding to the new diffusion potential; the latter eventually changes to an equilibrium potential as diffusion approaches completion.

Let a steady state of diffusion be set up in a region B separating two regions A and C whose compositions are maintained at constant values while diffusion proceeds at constancy of pressure and temperature (thermal effects of diffusion can always be supposed to be eliminated by suitably detailed systems of small scale thermostating). Let  $\dot{N}_i$  denote the number of gram ions flowing from A, across B, to C per second of ion  $i$  when a steady state of flow has been set up. Then the *resistance of passage* of ion  $i$  across B can be defined by

$$\rho_i = -\frac{\Delta\bar{\mu}_i}{\dot{N}_i} = -\frac{\Delta\mu_i + z_i F \Delta\psi}{\dot{N}_i} \quad (4)$$

where  $\Delta\bar{\mu}_i$  is written for  $(^B\bar{\mu}_i - ^A\bar{\mu}_i)$ , etc. In a steady state of flow  $\dot{N}_i$  is constant throughout B, even if B is not homogeneous throughout its length. Denoting the increments in  $\rho_i$ ,  $\Delta\bar{\mu}_i$ ,  $\Delta\mu_i$ ,  $\Delta\psi$ , and  $\dot{N}_i$  due to the formation of an adsorbed layer respectively by  $\Delta\rho_i$ ,  $\Delta\Delta\bar{\mu}_i$ ,  $\Delta\Delta\mu_i$ ,  $\Delta\Delta\psi$ , and  $\Delta\dot{N}_i$ , (4) gives

$$\Delta(\dot{N}_i \rho_i) = -\Delta\Delta\mu_i - z_i F \Delta\Delta\psi \quad (5)$$

When all the capacities to earth have had time to charge up a state of steady flow corresponds to zero flow of charge, so that  $\sum_1^s z_i \dot{N}_i = 0$  where the summation is over all the ionic species (1 . . .  $r$  . . .  $s$ ) in the system, and dissociating molecules are treated as composed of these ions. Substituting this into (5) and assuming that  $\Delta\rho_i$  is small and writing it as  $\delta\rho_i$ , etc., it is possible, since  $\sum_1^s z_i \Delta\dot{N}_i = 0$  and since *ex hypothesi*  $\Delta\Delta\mu_i = 0$  (1 . . .  $s$ ), to say

$$\Delta\Delta\psi = -\rho_e F \sum_1^s (z_i \dot{N}_i \delta \log \rho_i) \quad (6)$$

where  $\rho_e$ , the electrical resistance of B, is given by

$$\frac{1}{\rho_e} = F^2 \sum_1^s \frac{z_i^2}{\rho_i} \quad (7)$$

From (7), since  $\rho_i$  is positive,  $\frac{F\rho_e}{\rho_i} \geq \frac{1}{z_i^2 F}$  and this with (6) shows that

$$\Delta\Delta\psi = 0 \text{ (all } \delta \log \rho_i = 0) \quad (8)$$

and that if all the  $\delta \log \rho_i$  are zero except only  $\delta \log \rho_j$  that

$$|z_j F \Delta\Delta\psi| = |\Delta\Delta\bar{\mu}_j| \geq |\Delta\bar{\mu}_j| \cdot |\delta \log \rho_j| \quad (9)$$

For diffusion across a region where  $\Delta\bar{\mu}_j$  is not greater than 1 volt-Faraday and where ion  $j$  is a univalent ion with a value for  $\delta \log \rho_j$  of less than 0.001 while all other  $\delta \log \rho_r$  are zero the diffusion potential will alter owing to adsorption by less than 1 m.-volt.

If the thermodynamic argument (zero work for a closed isothermal reversible cycle) of equating the driving force on a gram ion of species  $i$  to  $-\frac{\partial\bar{\mu}_i}{\partial x}$  is accepted as valid under the non-equilibrium conditions of diffusion and if the mean velocity of a gram ion under unit force is  $l_i$  it is possible to write for the resistance to passage of ion  $i$  across a homogeneous region of cross-section  $A$  and thickness  $\delta x$

$$\delta\rho_i = -\frac{\delta\bar{\mu}_i}{\bar{N}_i} + \frac{\delta x}{Ac_i l_i} \quad (10)$$

where  $c_i$  denotes the concentration of ion  $i$  in moles cm.<sup>-3</sup>. Once in a steady state  $\bar{N}_i$  is constant and (10) can be integrated to give

$$\rho_i = + \int \frac{dx}{Ac_i l_i} \quad (11)$$

Expressions (9), (10), and (11) show that a thin adsorbed layer may give so small values to all the  $\Delta\rho_i$  terms that it cannot affect the diffusion potential. Physically speaking the adsorbed region can be so permeable as to operate on only a negligible fraction of the gradients of electrochemical potential and therefore it cannot alter the previously existing values for  $\Delta\psi$  and so  $\Delta\Delta\psi = 0$ . This conclusion is readily visualised in the case of a thin multilayer separating two aqueous phases since the fall of concentration across the membrane would tend to zero for the given boundary conditions and a permeable membrane. When the membrane separates two different phases the result has to be deduced in some such way as the above.

Expressions (6) to (9) only have a physical meaning of interest when the  $\rho_i$  terms can be interpreted by expressions (10) and (11) in addition to expression (4). For effusion into vacuo or for any saturation diffusion current the force on a particle is not given by  $\partial\bar{\mu}_i/\partial x$  which becomes infinite. Thus if the  $l_i$  are defined in the ordinary way in terms of the viscous resistance to motion of the particles expressions (4) and (11) give respectively an infinite and a normal value for  $\rho_i$ . In cases, therefore, of saturation diffusion currents it is possible for a thin membrane to have a negligible value for  $\delta \log \rho_i$  as judged by expression (11) and yet an appreciable value for  $\delta \log \rho_i$  as judged from expression (4), which means that an appreciable potential due to the membrane can appear. This can happen when the membrane is very permeable to ions and a saturation current of diffusing particles is flowing through it.

Though the potential of a battery is found to be independent of the resistance through which it is measured it appears that the amount that a membrane can affect a diffusion potential does depend on the resistance to passage that it offers to different ionic species. It is also interesting to note that the reduction of the resistance of an existing membrane by adsorption on it of a suitable substance can also affect  $\Delta\Delta\psi$ .

In the case of very thin membranes it is possible in theory to keep  $\delta \log \rho_i$  big by reducing  $\rho_i$ , that is by reducing the thickness of region B. In practice limits are set to how much  $\rho_i$  can be reduced first by the

difficulty of flowing solutions past a fragile membrane, so as to maintain the change in  $\bar{\mu}_i$  for the membrane to operate on, and secondly by the existence of viscous drag which reduces the rate at which changes in concentration due to diffusion can be compensated by the renewal of solution. Another way in which a very thin membrane can produce a diffusion potential is to maintain the concentration gradient by producing ions catalytically (enzymatically for living membrane) on one side and by destroying these ions catalytically on the other side.

### The Theory of Oil-Water Potentials.

It follows that the potentials observed at oil-water interfaces arise from phase boundary potentials and diffusion potentials and can only be contributed to appreciably by adsorption potentials in the special case of there being at the oil-water interface an adsorbed layer that sufficiently affects its resistance to passage of at least one ionic species. The potential is given to the accuracy of classical theory by

$$\psi_\beta - \psi_\alpha = - \sum_i \int_\alpha^\beta \left( \frac{t_i}{z_i F} \right) \left( \frac{\partial \mu_i}{\partial x} \right) dx \quad (12)$$

where  $t_i$  denotes the fraction of current carried by ion  $i$  in the given

region and may be written  $t_i = \frac{z_i^2 c_i l_i}{\sum_j z_j^2 c_j l_j}$ . The expression is exact in

the limiting case of true equilibrium, provided that the  $t_i$  refer to zero current density, and therefore deals precisely with reversible electrode potentials, Donnan potentials, and adsorption potentials at an interface that is completely impermeable to ions of all species. As previously pointed out <sup>6</sup> the relationship of the  $\mu_i$  to the concentrations  $c_i$  is more complicated in oil-water systems than in simple one-phase systems and will depend on the relative amounts of oil and water in different regions.

If the concentration of one ion,  $j$ , tends to zero,  $t_j$  tends directly to zero and  $\mu_j$  to log zero, so that  $t_j d\mu_j$  tends to zero. Thus an electrolyte diffusing into an oil cannot contribute to a diffusion potential once the concentration of its ions is sufficiently low compared to those of ions existing in the oil a long way from the phase from which the ions are diffusing.

Thus the potential difference between two aqueous drops of different composition is independent of the separation of the drops once this exceeds a critical distance. As the drops approach regions of diffusion potential in the oil become replaced by regions of diffusion potential in the aqueous phase. The latter regions at the concentrations generally used in practice generally give zero diffusion potential, since the aqueous phase is usually highly ionised compared with the oil and contains ions other than those of the diffusing electrolyte. Thus the first change of potential as the drops approach corresponds roughly to the removal of part of the diffusion potential in the oil and the effect is small since at great distances the diffusion potential in the oil is nearly swamped by the ordinary ions present in the oil. Further approach leads to the annihilation of more of the diffusion potential and at an increasingly rapid rate. On closer approach diffusion through the whole oil film becomes rapid enough to tend to equalise the concentrations in the aqueous



phases in contact with the two interfaces, so that the opposing phase boundary potentials tend to equalise. Finally as the diffuse double layers in the oil phase overlap the opposing and almost equal phase boundary potentials both fall to zero as the last traces of oil are removed.

If a large organic positive (negative) ion and a small inorganic negative (positive) ion diffuse from water into oil the phase boundary potential will in general make the oil take the sign of the charge of the big ion because the latter will generally have the greater solubility in the oil; this can be shown approximately from Born's<sup>8</sup> expression for the electrical contribution to the free energy of solvation of a spherical ion. As the electrolyte diffuses into the oil the smaller ion is likely to have the greater mobility so that the diffusion potential in this case is likely to be in the opposite direction to the phase boundary potential.

### Summary.

Thin layers of insoluble substances, permeable to at least one ionic species, cannot affect the electrical potential difference between two phases in equilibrium; they can only affect diffusion potentials between two phases when they offer sufficient change in the resistance to passage to at least one ionic species. An expression for the diffusion potential through a thin and permeable membrane in terms of the resistance to passage through it of different ions has been obtained.

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<sup>8</sup> Born, *Z. Physik*, 1920, 1, 45.

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## ADSORPTION POTENTIALS. PART II.—OIL-WATER POTENTIALS.

BY R. B. DEAN.

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Potential differences between oils and various aqueous solutions have been examined notably by Beutner, Cremer, and Hober<sup>1</sup> in an attempt to imitate and explain the steady potential differences found in living systems. Potential differences of corresponding magnitude to those found in living systems can easily be obtained by interposing suitable oil phases between electrolytes of different composition, and the fact that the penetration of large molecules into living cells follows closely the oil or lipid solubility of the molecule<sup>2</sup> has given support to the theory that the seat of bioelectric potentials lies in a lipid-like cell wall. However, the measurements of Cole<sup>3</sup> show capacities of the

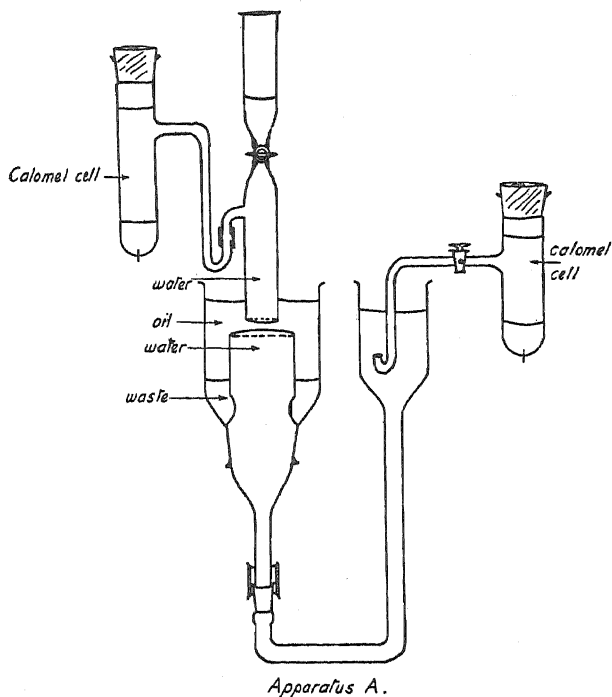
<sup>1</sup> Adam, *The Physics and Chemistry of Surfaces*, p. 359, Oxford, 1938. Beutner, *Physical Chemistry of Living Tissues*, etc., p. 192, London, 1933. Michaelis, *Hydrogen Ion Concentration*, Vol. 1, p. 183, Baltimore, 1926, for reviews and also Ehrensvärd and Sillén, *Nature*, 1938, 141, 789.

<sup>2</sup> Collander, *Trans. Faraday Soc.*, 1937, 33, 905.

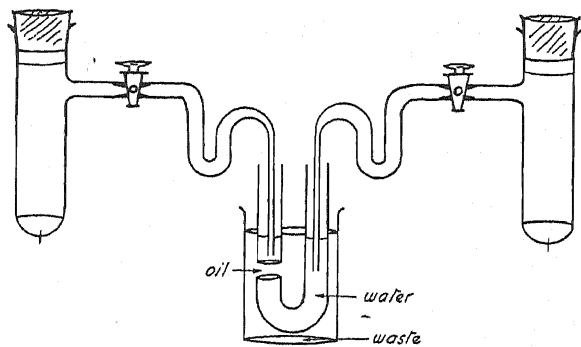
<sup>3</sup> Cole, *ibid.* Fricke, *J. Gen. Physiol.*, 1925, 9, 137.

high resistant part of the cell membranes of the order of  $2\text{--}3\ \mu\text{-Farads}$ ; provided polarisation capacities can be interpreted on an electrostatic condenser model this corresponds approximately to the thickness of a single monolayer. Again Dervichian and Macheboeuf<sup>4</sup> have measured the quantity of oil in red blood cell ghosts as sufficient to cover the cell with a layer one molecule thick. Since there is no justification for assuming that monolayers will have the same electrical properties as an oil in bulk the following experiments on interfacial potentials between oils and water are of interest.

Baur and more recently Ehrensvärd and Sillén held that potentials at oil-water interfaces were the result of adsorption at the interface. In the previous paper<sup>5</sup> it has been shown that adsorption cannot permanently alter the potential between two phases in equilibrium nor can it affect diffusion potentials unless the adsorbed phase has a high resistance comparable to that of the bulk phases. In this paper the electrical properties of some adsorbed layers have also been studied as well as certain diffusion potentials in oil-water systems and all the observations support the conclusions of the previous paper.



Apparatus A.



Apparatus B.

FIG. 1.

<sup>4</sup> Dervichian and Macheboeuf, *Compt. Rend.*, 1938, 206, 1511.

<sup>5</sup> Dean and Gatty, *this volume*, p. 161.

### Methods.

The potential differences between two aqueous phases separated by an oil were measured between a hanging drop of water and the surface of water in an overflow vessel submerged in an oil lighter than water such as alcohols, ethers, and esters. In apparatus A (Fig. 1) the upper drop was 16 mm. in diameter at the end of a tube fitted with a filling stop-cock and side tube connection for a calomel cell. The lower tube was 4 cm. in diameter with ground edges so that the surface could be cleaned by sweeping with flame cleaned brass barriers so that a small drop containing the surface contaminants was swept over the edge. The upper drop was cleaned by allowing several drops to fall into the waste chamber. Each drop expanded the surface about three times and removed two-thirds of the maximum surface, thus ten drops should effectively remove surface contaminants that do not appear from the bulk phases. In passing it may be noted that water drops falling through oils exhibit very clearly the small following drop found by Guye and Perrot.<sup>6</sup>

Apparatus B had a J tube 10 mm. in inside diameter as the lower vessel and a shorter I tube of equal diameter above it for the hanging drop. Water was kept in the tubes by surface tension and hydrostatic pressure of the oil. The distance between the drops could be varied by moving the J tube. The lower surface was cleaned by running in water from a separating funnel so that a large drop formed before falling off into the waste water at the bottom of the beaker containing the oil. The hanging drop was cleaned just as in apparatus A.

The aqueous solutions used were shaken with the oil, allowed to separate and then filtered before using in an attempt to achieve equilibrium of electrolyte between the two phases. In every case the concentration stated refers to that in the water before shaking with the oil and no attempt was made to determine what fraction of the electrolyte was actually in the oil, but the electrical conductivities show that it must always have been small. Electrical connection to the oil was made through calomel half-cells with the experimental solution sucked back into the side tubes to give reproducible liquid-liquid junction potentials. Potentials were read by balancing on a standard potentiometer using a Lindeman electrometer as null instrument. Resistance was measured by applying a potential in series with a high resistance through separate polarising electrodes in the water and measuring the change in potential across the calomels. The exact formula for converting the resistance between two drops into a specific resistance was not applied since orders of magnitude only were required. In apparatus A the resistances with the drops 1 cm. apart are recorded and with apparatus B the resistance with them 5 mm. apart, and the resulting figures have been used to give approximate values to the specific resistance. The advantage of measuring in bulk liquid is that errors due to surface conductivities in the vessel, which may be considerable with high resistant oils, are eliminated.

### Results.

#### Preliminary Observations.

The potential difference between two clean drops of the same composition was not always the same as when the drops were coalesced to form a continuous aqueous connection between the calomels. This departure from the ideal case was most marked with high resistant oils and in the case of oils of more than  $10^{11}$  ohms specific resistance (these resistances are similar to those of air ionised by radioactive sources. See Part III) made measurements impossible. Also with these oils stray potentials caused by opening the shorting key take a long time to leak away to

<sup>6</sup> Guye and Perrot, *Arch. Sci. Phy. Nat. (Geneva)*, 1903, **15**, 178.

earth. With lower resistant oils the base line potentials were usually constant to a few millivolts although they varied somewhat with temperature and separation of the drops in a way that suggested that they might be due to incomplete equilibrium between the electrolyte and the oil.

Proteins were spread at a clean interface either by dropping the dry powder through the oil or by attaching it to a moist glass fibre which could be passed through the oil to the interface. If powdered  $\text{Bi}_2\text{O}_3$  is dusted on the upper oil surface it sinks to the interface and behaves like talcum at the air water interface showing the rate of spreading which was sometimes nearly as quick as in air and never less than 4 cm. sec.<sup>-1</sup>. Best results with interfacial egg albumen films were obtained near pH 3. Dry powdered dyes insoluble in the oil could be brought into either drop by attaching to a moist glass fibre although they were usually dissolved in the aqueous solution and injected into either drop through the oil or into the open end of the I tube in apparatus B.

### The Resistance of Thin Films.

Attempts to measure the change in resistance of the system when albumen was spread at one interface always showed no change to the limits of experimental error which reduced in the case of amyl alcohol to only 1000 ohms.

### Diffusion Potentials.

If two clean water drops are pressed together the oil layer between them breaks after a short time, depending probably on the viscosity of the oil. If the drops have interfacial films formed by cholesterol in the oil (octyl alcohol) forming a complex with digitonin in the water<sup>8</sup> they will be stable in contact for several minutes. If, however, a polarising potential be applied across the oil the bubbles will coalesce after a shorter time. Fig. 2 shows the relation of the average breaking time to applied voltage for one experiment.

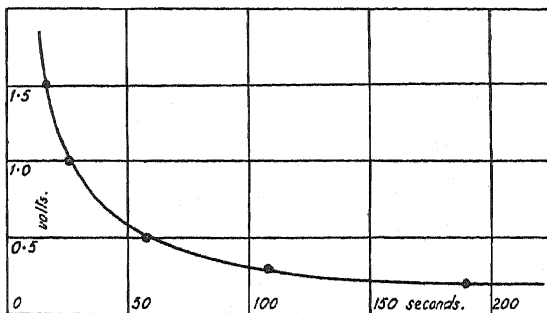


FIG. 2.

The breaking times fluctuate considerably about the averages which are significant to about 20 per cent. The resistance of these layers of octyl alcohol between two drops of molar KCl averages 50 megohms when measured with a polarising potential of 0.1 volt but also fluctuates with much the same dispersion as the breaking times. This suggests that the dispersion in the breaking times is a result of the varied resistances in the oil which were probably caused by uncontrolled factors in the formation of the thin layers. The large variations suggest that the resistance of the interfacial complex layers is small compared with that of the oil between. Preliminary calculations show that the system has a time constant of the order of 100 seconds which, with a resistance of 50 megohms indicates a capacity of 20  $\mu$ -Farads, if the breakdown occurs when a definite potential is built up

<sup>8</sup> Gatty (*in the press*).

across the capacity. These results are entirely preliminary, however, and further work on these systems is planned.

If the drops are protected by an elastic film they are more stable. Egg albumen films at their own spreading pressure at pH 3 form stiff gels as can be seen by blowing a jet of oil on the  $\text{Bi}_2\text{O}_3$  particles on the surface. Two water drops protected by albumen films can sometimes be stuck together to form a stable visible skin between the drops. Electrical polarisation showed this skin to have a resistance of less than 1 ohm  $\text{cm}^2$  which is equivalent to 1 mm. of M./1 KCl, 10 A. of butyl acetate, or only 0.2 A. of octyl alcohol assuming the resistance of the oil near a water interface to be equal to that in the bulk phase. This suggests that there is no continuous film between the drops even though they could sometimes be separated. In view of the much higher specific resistance of "Nujol" it is doubtful whether any oil remained between the drops even though they could be separated quite easily. Probably the area of contact increased slowly as the oil was squeezed out. When the drops stuck together as usually happened in butyl acetate drawing the supporting tubes apart makes evident the exact area stuck together and its diameter could be estimated by comparing its apparent diameter with the apparent diameter of the supporting tube by means of an external scale. Rupturing the film between the drops with a glass needle produced no change in the resistance of the circuit thus setting an upper limit to the resistance of the two surface layers of albumen.

There is no potential difference across the double egg albumen layers nor do they appreciably retard the diffusion of dyes or produce potentials when dyes diffuse through them. Gatty<sup>7</sup> has found that thick "multi-layers" of egg albumen do retard the diffusion of dyes and other workers have reported diffusion potentials in proteins that differ from those in water. The protein layers under discussion are too permeable to affect the diffusion potential of substances according to the theory of the preceding paper.

In neutral oils inorganic salts have only small diffusion potentials but if a dye dissociated into a large organic ion and a small inorganic ion such as methylene blue chloride or sodium eosinate is put in one drop a large potential difference develops between the drops. The water containing the dye becomes negative in the case of methylene blue chloride and positive in the case of the eosin. Using methylene blue in 0.01 M.  $\text{K}_2\text{SO}_4$  and octyl alcohol in which the dye is relatively insoluble potentials of 70 to 80 millivolts were obtained which remained substantially constant for 24 hours. In butyl acetate in solutions of 0.01 M.  $\text{K}_2\text{SO}_4$  potentials of 60 m.volts were obtained. Eosin in  $\text{K}_2\text{SO}_4$  with butyl acetate gave potentials initially of 100 m.-volts but the dye could be seen diffusing into the oil and the potential fell to 50 m.-volts in 25 minutes.

When two drops, one containing a dye, were touched together, the potential difference vanished, and when the drops were separated again as is sometimes possible, the potential built up again to its previous value. Methylene blue gave similar diffusion potentials whether or not the interface was covered with albumen and since a double layer of albumen does not retard the diffusion of dyes it should not have any influence on the diffusion potential (Part I). If, however, the potential difference were caused by adsorption one would expect large differences depending on the substance initially present at the interface. When the drops are brought close together with digitonin cholesterol as the protecting film so that a thin film of oil remains between them, the dye diffusion potential reaches higher values.

The above results can best be explained by the theory given in the preceding paper which depends on the greater solubility of the organic ion in the oil, the greater mobility of the small inorganic ion (assumed not to be heavily solvated), and the ultimate swamping of the potential due to diffusion of dye by the ions originally present in the oil. The

theory leads to the purely schematic potential-distance curve of Fig. 3 which fits in well with the observed facts. In an oil with a specific resistance of  $10^9$  ohms one would expect quite thick Gouy layers even if all the inorganic ions were to remain on the aqueous side of the interface which corresponds to the dye adsorbing on the oil. With highly resistant oils completely dissociated dyes would not be expected to diffuse very fast because of the difficulty of dragging attendant ions of the opposite sign. That eosin does in fact diffuse as an ion into butyl acetate is shown by the fact that its solutions in that solvent are fluorescent while acidified eosin where the dye is undissociated is not fluorescent.

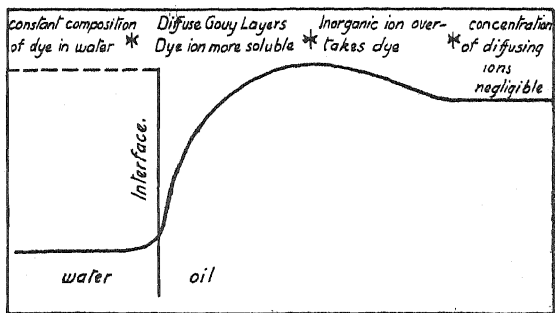


FIG. 3.

When the oils are better conductors, as is the case when they are shaken with more concentrated or more oil soluble electrolytes, the dye diffusion potentials are smaller. In 0.01 M.  $K_2SO_4$  against butyl acetate eosin gave a maximum of 100 m.volts and in 1 M. KCl only 50 m.volts. Methylene blue is insoluble in strong salt solutions and does not give consistent results. The effect is probably due to the smaller transport numbers for the dye ion and its attendant ion so that the diffusion potential is swamped by the other ions.

### Adsorption Changes in Potential.

When the interfacial layer is changed, either by spreading an albumen film or by adsorbing tannic acid on an albumen film from aqueous solution there is a quick change in the potential. Spreading albumen usually makes the water more negative while adsorbing tannic acid produced the opposite change which is qualitatively the same as found by Schulman and Rideal<sup>8</sup> at the air water interface. However, these potentials decay to zero in an approximately exponential manner with a time constant (i.e., time to fall to 1/e of the maximum) that depends primarily on the resistance of the oil. Table I shows the resistance, greatest maximum potential observed, and mean time constant when albumen was spread at a given oil interface. The maxima were measured about 30 seconds after spreading.

When the interface was swept removing a small drop of water there was a potential change of the same sign and approximately the same magnitude and time constant as when albumen was spread at the interface. The potential change was independent of whether or not albumen was present on the interface. In only one case was a significant difference observed, that of iso-propyl ether, and there the protein potential took about 3 minutes to reach its maximum after spreading on 0.01 M.  $K_2SO_4$  and less than 30 seconds after sweeping the surface.

Polarising for 1 minute at 1.5 volts produced residual potentials of the same order as cleaning or spreading but in the case of octyl alcohol these residual potentials took about half as long to decay. The decay was strictly not exponential and longer periods of polarisation lead to higher potential differences taking longer to decay.

<sup>8</sup> Schulman and Rideal, *Proc. Roy. Soc., B.*, 1937, 122, 29.

At the interface between a conducting oil and water there will be an oriented layer of dipoles in the oil with the polar groups turned towards the water. This produces a difference of electrical potential between the two phases but both phases and the interface are electrolytically conducting and so this potential difference can be neutralised by the separation of pairs of ions across the interface to form a diffuse Gouy layer in each phase. Short range forces can superpose a separation of charge in either phase alone and so cause an effect which may either oppose or support the original dipole field and has to be compensated for by separation of charge across the interface. Orientation of the dipoles can take place in less than one second but the neutralising layers will take more time to build up since they involve movements of ions in the oil. The time required to neutralise the dipole field will in general be a function of the concentration of ions in the oil since if the layer is dilute it must extend further to produce an equivalent potential. It also depends on the viscosity of the oil. Since the specific resistance also depends on the concentration of ions and the viscosity the time of decay of potential should be closely correlated with the resistance of the oil as is shown in Table I.

TABLE I.

Oil.	Aqueous Solution.	Resistance of Oil in Megohms.	Time Constants (mins.).	Maximum Potential.
Valeric acid .	0.01 M. $K_2SO_4$	0.05	—	0 mv.
Amyl alcohol .	0.01 M. $K_2SO_4$	2	0.03	+ 3 mv.
Butyl acetate .	0.01 M. $K_2SO_4$	40	4	-32 mv.
Ethyl ether .	0.01 M. $K_2SO_4$	1,000	5	-40 mv.
Amyl butyrate .	0.01 M. $K_2SO_4$	1,000	10	-30 mv.
Amyl acetate .	0.01 M. $K_2SO_4$	1,300	8	-40 mv.
Anisole .	0.01 M. $K_2SO_4$	5,000	12	-25 mv.
Octyl alcohol .	0.01 M. $K_2SO_4$	6,500	27	-35 mv.
Isopropyl ether .	0.01 M. $K_2SO_4$	7,000	30	-35 mv.
Octyl acetate .	0.01 M. $K_2SO_4$	12,000	12	-45 mv.
Amyl acetate .	0.01 M. $(C_2H_5)_4NCl$	3,000	12	-20 mv.
Amyl acetate .	0.01 M. $K_2SO_4$	1,300	8	-40 mv.
Octyl alcohol .	0.1 M. $NaI$	180	3	-12 mv.
Octyl alcohol .	1.0 M. $KCl$	5,000	2.5	-20 mv.
Octyl alcohol .	0.01 M. $K_2SO_4$	6,500	27	-35 mv.

When the interface is swept by a barrier the diffuse double layers are removed leaving the surface charged by the oil dipoles and water dipoles which orient themselves very rapidly. There should therefore be a potential surge and decay to zero as the neutralising double layer reforms just as when a protein is spread. Since a spreading monolayer has been shown by Schulman and Teorell<sup>9</sup> to carry with it a relatively thick layer of water and presumably also carries an oil layer as well, Frank<sup>10</sup> suggested that the potential observed on spreading albumen might be due almost entirely to its mechanical displacement of the existing double layer if the potential due to the protein was less than that due to the oriented oil molecules themselves. Since tannic acid adsorbing from a solution, so that it does not disturb the oil, also produces a potential change followed by decay the mechanical disturbance of the double layers cannot be the only cause of such potentials.

<sup>9</sup> Schulman and Teorell, *Trans. Faraday Soc.*, 1938, 34, 1337.

<sup>10</sup> Frank (*private communication*).

### Summary.

A method for investigating the electrical properties of oil-water interfaces is described and details of the spreading of egg albumen at these interfaces are given. Two protein monolayers have a resistance of less than 1 ohm cm.<sup>-2</sup>. Thin oil layers between cholesterol digitonin complexes and the complexes themselves can be broken down by application of polarising current. The spreading of a monolayer at these interfaces produces a temporary surge of potential that subsequently disappears with a time constant that is related to the conductivity of the oil phase. Monolayers do not produce permanent changes either of equilibrium or of diffusion potentials in accordance with the theory of Part I. The diffusion potentials of oil-water systems, though unaffected by monolayers, are considerable and have been investigated as a function of the separation of two water drops in the oil. The results indicate a larger phase boundary potential and a smaller diffusion potential through the oil. At very small distances from the aqueous phase the oil diffusion potential gets swamped by other ions in the oil. For thinner layers of oil the diffusion potential gets smaller in accordance with the theory of Part I and ultimately it vanishes as the layer gets very thin.

The author would like to thank Professor E. K. Rideal, F.R.S., and Dr. J. H. Schulman, very much for continual advice and encouragement throughout the course of this work.

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## ADSORPTION POTENTIALS. PART III. — AIR-WATER POTENTIALS.

BY R. B. DEAN AND O. GATTY.

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In a previous paper <sup>1(a)</sup> it has been shown that the spreading at a plane interface between two phases in thermodynamic equilibrium of a monolayer insoluble in both phases and permeable to at least one ionic species whilst producing a transitory surge of potential cannot alter the interfacial potential difference under equilibrium conditions. If diffusion is taking place between the two phases the diffusion potential can only be affected if the monolayer sufficiently affects the resistance to passage of at least one ionic species. This theory is supported by experimental observations at oil-water interfaces. <sup>1(b)</sup> It was shown in Part I that a thin membrane might have a low value for  $\delta \log \rho_i$  as judged by expression (11) for  $\rho_i$  but a high value for  $\delta \log \rho_i$  as judged by expression (4) and therefore to show an appreciable potential due to the layer although the latter was freely permeable to ions since they were diffusing in a saturation diffusion current through it in one direction. This can be visualised in the following kinetic picture. The potential difference between two phases is altered when a layer of oriented dipoles is interposed between them but the change in potential difference is eventually compensated. The compensation is due to separation of

<sup>1</sup> Dean and Gatty, *This volume*, 1(a), Part I, and 1(b), Part II.



electric charge (*a*) across the interface, (*b*) in phase I, and (*c*) in phase II. If there were no short range forces and if the dipole field were smoothed to correspond perfectly to that of a parallel plate condenser the only separation of charge would be across the interface. Any mechanism that instantaneously removed all electric charges from the region of the interface would prevent the compensation taking place. Complete compensation could not be obtained if there was a mechanism which instantaneously removed all the electric charges in one of the two phases from the region of the interface. Systems of this latter type would, therefore, show only incomplete compensation of the potential difference due to the dipole field; moreover, a number of physical mechanisms might be expected to produce a system of this type.

Monolayers spread at the air-water interphase are known to affect the potential difference between the two phases. This can occur as an equilibrium phenomenon if the air is not ionised by a radioactive source since the ionisation due to cosmic radiation can be treated as negligible. Under these conditions ions do not escape in appreciable numbers from the aqueous into the aerial phase so that the air and the interphase together constitute a barrier that is effectively impermeable to ions. A genuine adsorption potential is set up which can be measured by the volta plate method <sup>2</sup> or by a vibrating plate modification of this <sup>3</sup> or by a flowing solution method; <sup>4</sup> in all cases a condition of zero potential gradient across the air gap being found by the observations.

More usually these potentials are measured through air made conducting by ionisation from a radioactive source. Equilibrium adsorption potentials could still give potentials in this case but only if the monolayer was sufficiently non-conducting (absolutely so for complete equilibrium). This latter hypothesis will be shown to be unsatisfactory on experimental and theoretical grounds. Similarly the hypothesis that the observed potential is a diffusion potential through the monolayer can be rejected. The explanation put forward is that the removal of the potential due to the monolayer, which should occur in the equilibrium case, necessitates the presence of a portion at least of a double layer in the aerial phase but that the ions in the air are so few that in the double layer they are all subjected individually to image forces which draw them into the aqueous phase. The image forces are too powerful to allow any compensating double layer to build up in the aerial phase and therefore the potentials measured through ionised air agree with those obtained in other ways.

The current-voltage curves were obtained from two sources of RaD plus Po and from one source of mesothorium that were in current use in the laboratory. Their respective saturation currents were  $1.7 \times 10^{-10}$ ,  $8.21 \times 10^{-11}$ , and  $8.44 \times 10^{-11}$  amps. irrespective of the direction of current flow. The actual resistance for low potential differences of the air-gap is about  $10^{11}$  ohms and the specific resistance of the air is  $9 \times 10^{11}$  ohms cm.<sup>+1</sup>. The coefficient for recombination of ions in air is given as  $1.6 \times 10^{-6}$  by J. J. Thomson and G. P. Thomson considering

<sup>2</sup>Guyot, *Ann. Physique*, 1924, 2, 506. Garrison, *J. physik. Chem.*, 1925, 29, 1517.

<sup>3</sup>Yamins and Zisman, *J. Chem. Physics*, 1933, 1, 656. Porter, *J.A.C.S.*, 1937, 1884.

<sup>4</sup>Bichet and Blondlot, *J. Physique*, 1883, 2, 533. Kenrick, *Z. physik. Chem.*, 1896, 19, 625. Frumkin, *ibid.*, 1924, 109, 34; 111, 190; 1926, 123, 321. Frumkin, *Acta Physicochem. U.R.S.S.*, 1935, 2, 1. Frumkin and Donde, *Z. physik. Chem.*, 1926, 123, 329.

values up to 1928, as  $1.7 \times 10^{-6}$  by Schemel<sup>5</sup> and as  $0.8$  to  $0.9 \times 10^{-6}$  by Marshall.<sup>6</sup> Taking Schemel's value the numbers of positive ions  $\text{cm}^{-2}$  are given respectively by  $2.51 \times 10^7$ ,  $1.75 \times 10^7$ , and  $1.77 \times 10^7$ , while Marshall's value give the numbers respectively as  $3.55 \times 10^7$ ,  $2.47 \times 10^7$ , and  $2.50 \times 10^7$ . Flowing the saturation current of  $8.21 \times 10^{-11}$  amps. for 33 hours 8 minutes or 119,280 seconds affected the potential, at zero current density of a monolayer of stearic acid on sodium phosphate buffered to  $\text{pH}$  7.2, by less than 1 millivolt. If, therefore, the surface were behaving as a perfectly insulating condenser, its capacity would have to exceed 9794  $\mu\text{F}$ . If the film had infinite resistance charge would slowly distribute itself over the whole surface of the film which was 216  $\text{cm}^2$ . Thus the monolayer can only behave as a perfectly insulating condenser if its capacity exceeds 45.34  $\mu\text{F}$ .  $\text{cm}^{-2}$ . A capacity of this magnitude is most unlikely for a monolayer of stearate since it corresponds in the case of a parallel plate condenser to a separation of only some 0.2 Å. So-called "polarisation capacities" which greatly exceed ordinary parallel plate condenser capacities are observed at some metal-solution interfaces, they probably arise from concentration polarisation and a corresponding change in the reversible electrode potential. These capacities only arise at conducting interfaces. It seems, therefore, that the monolayer cannot be entirely impermeable to ions. In addition since the radioactive source was very close to the surface of the trough the resistance to the edges must have been considerable compared to the resistance to just below the wire electrode, so that the lower limit for the capacity could well be multiplied at least by a factor of 2.

Additional arguments against almost completely impermeable surface films are the electrical resistance data for monolayers spread at oil-water surfaces which never give high resistances,<sup>1(b)</sup> the work of Rideal<sup>7</sup> which shows that at ordinary surface pressures monolayers are still fairly permeable to water vapour, and the fact that even at a compression of 80 dynes (corresponding to zero surface tension) a hole 64 Å.<sup>2</sup> can be expanded with only 12.8 kT of compressional work. Such a hole should let air ions through into the aqueous phase.

If a glass or quartz tube encloses the air electrode and dips through the monolayer into the solution the potential can be affected by passing polarising currents and the resulting change decays with time. This behaviour is what would be expected if the monolayer behaved like a capacity in the polarising experiment described above. The results with the tube can also be obtained with glass tubes standing on metal plates and presumably involve the charging and discharging of capacities to earth and the appearance of surface conductivity on substances subjected to ionising radiations.

If it is accepted that the film is not a very high capacity of very high insulation Ohm's law shows that its resistance is less than  $1.22 \times 10^7$  ohms or less than  $2.64 \times 10^9$  ohms  $\text{cm}^2$  since the saturation current produced less than 1 m.volt.

If the film does not behave like a perfectly insulating condenser the potential cannot be an equilibrium adsorption potential. The possibility of its being a diffusion potential has to be investigated. Leaving a stearate film on sodium phosphate at  $\text{pH}$  7.2 and a RaD plus

<sup>5</sup> Schemel, *Ann. Physique*, 1928, **85**, 137.

<sup>6</sup> Marshall, *Physic. Rev.*, 1929, **34**, 618.

<sup>7</sup> Rideal, *J. Physic. Chem.*, 1925, **29**, 1585.

Po electrode enclosed in a quartz tube dipping through the monolayer into the solution the potential changes by less than 1 m.-volt, that is, by less than  $\frac{1}{3}$  per cent. of the potential due to the stearate, in 69 hours. On the hypothesis that the monolayer potential decays exponentially with time due to diffusion this gives a time constant of some  $7.5 \times 10^7$  seconds. Diffusion processes have error function decay processes, but the above value can be used to obtain the order of the diffusion constant into 2 cm. of air or into 10 Å. of film that is necessary to give a time constant of  $7.5 \times 10^7$  seconds. The values in  $\text{cm.}^2 \text{ sec.}^{-1}$  are respectively  $5.3 \times 10^{-8}$  and  $1.3 \times 10^{-22}$ . That for an organic molecule of molecular weight 180 into air is about  $2 \times 10^{-2}$  and no constant as low as  $10^{-21}$  has yet been measured even for one solid metal into another. It seems, therefore, that the only possible diffusion process is that of air ions into the water since diffusion saturation would only be reached when the radioactive source had decayed which RaD does with a half-life of 16.5 years.

In any case the diffusion of water vapour can hardly produce the potential since diurnal variations of temperature in the case of the monolayer enclosed by the quartz tube should reverse the net rate of condensation or evaporation. The monolayer can hardly maintain its potential and yet itself evaporate. Born's expression for the electrical contribution to the free energy of solvation of ions shows that energies of activation in excess of 20,000 calories are needed to transfer ions from the aqueous to the aerial phase. Again Lenard<sup>8</sup> showed that the mere rubbing of a liquid against a gas when a rapid jet is flowing produces no ballo-electricity; nor does the latter appear when a liquid disappears without spray. He therefore inferred that the double layer lies entirely in the aqueous phase. Finally no appreciable current apart from that due to ionisation by cosmic radiation flows between an electrolytic solution and a metal plate in the air just above it provided the applied potential is low enough. Thus evaporation of electrolyte and of the film itself seem to be excluded. Water evaporation is most unlikely as the potential would have to be independent of the rate and direction of evaporation and vanish only at zero net rate. The only alternative is, in fact, the air ions as diffusing particles.

The change in interfacial potential difference due to a monolayer is independent of the strength of the radioactive source. This has been tested directly by Schulman over a twofold change in strength; again workers in various laboratories with different sources get the same values for monolayer potentials. Lastly, the monolayer potential is independent of the distance from the surface of a given source provided the distance is small enough to prevent the potential being measured in part through alternative paths to earth (*i.e.*, to the walls of the box through the air or by surface conduction). Again the potentials agree with those obtained by the methods that do not employ ionised air. *Thus the potential cannot be accounted for by any reasonable diffusion processes any more than by the hypothesis of an insulating monolayer.*

The use of probe electrodes shows that the specific resistance of the air near the solution surface and near the RaD plus Po electrode is greater than that of air further removed from the electrode. The procedure is to apply one volt between the Po plus RaD electrode and a calomel electrode in the solution and to observe the potential taken up by a

<sup>8</sup> Lenard, *Sitzungsber. Heidelb. Akad.*, 1914, 28 Abt.

probe electrode in the air between the two polarising electrodes. Quantitative work is difficult owing to stray capacities and the possibility of surface conductivity over the probe but it was found that about  $\frac{1}{3}$  of the applied potential was recovered in 4 mm. of air,  $\frac{1}{3}$  in  $\frac{1}{2}$  mm. of air between the probe electrode and the solution, and  $\frac{1}{3}$  in the  $\frac{1}{2}$  mm. of air between the probe electrode and the RaD plus Po electrode.

The results with the probe electrode and the agreement of the values of monolayer potentials observed with and without radioactive sources suggest that the potentials due to the monolayer persist because no ionic double layer can be built up in the aerial phase. Both the RaD plus Po electrode and the solution surface it seems are "condensing electrodes" in the sense that any air ion that hits the surface does not return to the air until it has lost its charge. At the metal electrode the discharging probably occurs by electron transfer. In the aqueous phase the ions, if they do not recombine directly, probably release hydrogen and oxygen since the ionisation potentials of  $O_2$ ,  $N_2$ ,  $CO_2$ , and  $H_2O$  are respectively 13, 16.5, 14.4, and 13 volts while entering a medium of dielectric constant 80 can hardly be supposed to reduce their electrical energy by more than 4 electron volts. Thus the air ions of either sign should possess ample energy to discharge  $H_3O^+$  and  $OH^-$ .

For the observed behaviour to be explained it is sufficient that the concentration of cations and anions in the air phase be sufficiently low in the air directly outside the film so that no back electromotive force to neutralise the potential difference due to the film can ever be built up. The film and aqueous phase have to suck in ions from the air as fast as they diffuse up to it and this has to be done irrespective of the sign of the charge carried by the ion. A system of such a type is in such gross disequilibrium that it can have zero resistance to the passage of ions in one direction, let no ions pass the other way, and yet show a potential as has been pointed out in Part I and in the Introduction to the present paper. Since it is assumed that air ions cannot remain in the air near the film in order to reduce the monolayer potential to zero the hypothesis amounts to saying that every ion that hits the surface gets discharged and that there is no appreciable back reflection of ions of either sign; otherwise an appreciable back electromotive force would eventually build up and reduce the monolayer potential to zero.

This hypothesis is reasonable since it is to be expected on electrostatic grounds. A point charge of magnitude  $e$  when at a perpendicular distance  $r$  from an infinite plane has a potential energy given by

$$U = + \frac{e^2}{4D_a r} \left( \frac{D_a - D_s}{D_a + D_s} \right) \quad (1)$$

where the ion is in a medium of dielectric constant  $D_a$  and the other side of the infinite plane there is an infinite region of dielectric constant  $D_s$ . If an infinite slab of dielectric of thickness  $a$  and dielectric constant  $D_f$  is inserted between the charge and the medium of dielectric constant  $D_s$  the potential energy of the point charge can be expressed as arising from an infinite number of images as

$$U = + \frac{e^2}{4D_a} \left[ \frac{\alpha}{r-a} + \frac{\beta}{r} (1 - \alpha^2) + \frac{\beta^2 \alpha}{r+a} (1 - \alpha^2) + \frac{\beta^3 \alpha^2}{r+2a} (1 - \alpha^2) + \frac{\beta^4 \alpha^3}{r+3a} (1 - \alpha^2) + \dots \right] \quad (2)$$

where  $\alpha = \frac{D_a - D_f}{D_a + D_f}$  and  $\beta = \frac{D_f - D_s}{D_f + D_s}$ .

The potential energy for an oil film of thickness 20 Å. and of dielectric constant 2 separating a point ion in air from an aqueous solution of dielectric constant 80 is given by expression (2) as :

$$\begin{aligned} U &= -0.04 \text{ electron volts at } 100 \text{ Å. from the film (} r \text{ } 120 \text{ Å. and } a \text{ } 20 \text{ Å.).} \\ &= -0.51 \text{ electron volts at } 3 \text{ Å. from the film.} \\ &= -1.32 \text{ electron volts at } 1 \text{ Å. from the film.} \end{aligned}$$

Since the mean free path of the ions is not less than 100 Å. the ions that come within 3 Å. of the outer surface of the hydrophobic portion of the molecules are liable to have fallen without collision through some 0.5 electron volts. This field works on ions of either sign since their mean separation is of the order of  $(2 \times 10^7)^{-\frac{1}{3}}$  cm. or 0.0037 cm. which is great compared to 100 Å.

Use of the point charge model for the ion is not valid at distances less than 10 Å. but it appears that by falling in to a distance of 1 Å. the point ion would have acquired 1.32 electron volts. The dipole field of  $\omega$ -bromohexadecanoic acid at the air-hydrocarbon chain interface may conceivably amount to -1.15 volts (air negative) and so oppose the entry of positive ions from the air. If this field builds up linearly from 4 Å. to 1 Å. away from the hydrocarbon surface it would not offer sufficient opposition appreciably to delay the entry of positive ions into the paraffin. Once inside the paraffin the image forces continue to suck ions into the aqueous phase. The image force on an ion in an infinite medium of dielectric constant 2 at 3 Å. from an infinite medium of dielectric constant 80 is  $3.98 \times 10^7$  electron volts cm.<sup>-1</sup> while a uniform dipole field producing 600 m.-volts over 3 Å. produces only  $2 \times 10^7$  electron volts cm.<sup>-1</sup> in the region of the dipole and outside the dipole the field approximates to zero. If, therefore, the dipole field operates over some 3 Å. or less it is evident that point charge ions must all be sucked into the electrolyte through surface films irrespective of the sign of the charge that they carry. This follows since monolayer potentials of 1 volt are seldom observed, since these potentials are usually situated close to the aqueous phase rather than at the air-hydrocarbon interface and so are in a region of more intense image forces, and since the energy to produce a hole 64 Å.<sup>2</sup> in the most compressed film possible is only 12.8 kT or 0.32 electron volts.

Owing to the aqueous phase being an electrolytic conductor the image forces used in the above calculations become screened since an ionic atmosphere is set up which tends to reduce the polarisation which leads to the image effect. Wagner<sup>9</sup> and Onsager and Samaras<sup>10</sup> have made approximate evaluations of the screening forces which make the image forces fall away exponentially with distance. For distances less than 10 Å. this effect is not large in M./100 solutions or at greater dilutions. Their work, however, applies only to the case of ions (as opposed to images) in the aqueous phase and screening should be less in the aerial phase.

It might be objected that the model of a point ion is unsatisfactory even to a first approximation and that a spherical ionic model should be adopted. Born's<sup>11</sup> expression for the electrical contribution to the free energy of solvation of an ion is only approximate but is given by

$$U_e = \frac{e^2}{2r} \left( 1 - \frac{1}{D} \right) \quad . \quad . \quad . \quad . \quad (3)$$

<sup>9</sup> Wagner, *Physik. Z.*, 1924, **25**, 474.

<sup>10</sup> Onsager and Samaras, *J. Chem. Physics*, 1934, **2**, 528.

<sup>11</sup> Born, *Z. Physik*, 1920, **1**, 45.

where  $r$  is the radius of the ion. For  $D = 80$  and  $r = 3$  A.,  $U_0$  is 2.4 electron volts and for  $r = 5$  A.,  $U_0$  is 1.4 electron volts. Owing to the weak image forces repelling ions from the air-water interface when the ions are in the aqueous phase it is evident that most of this energy change takes place as the ion moves through the aerial phase up to the interface. Thus the spherical conductor of radius  $r$  is a model which also predicts that air ions of both signs will be sucked into the aqueous phase against the potential differences met with at these interfaces in actual practice.

The difficulty of interpreting air-monolayer potentials on any picture together with the above semi-quantitative arguments seem to establish the hypothesis of these surfaces as "condensing electrodes."

A corollary of the above work is that it is not possible to obtain electrocapillary curves for air-monolayer-aqueous phase systems since the low resistance of the surface film means that a negligible fraction of an applied potential difference is located at the interface. For aqueous solution-mercury systems almost the whole resistance can be located at the interface in suitable solutions and so big potential gradients are possible at the surface even though the resistance of the latter is less cm.<sup>2</sup> than that of the air-gap in air-water systems.

### Summary.

Air-monolayer-aqueous solution interfaces attract ionised air particles and any of these hitting the surface condense and get discharged before returning to the aerial phase. It follows that no compensating double layer can build up in the aerial phase in order to compensate for the field set up by an oriented layer of dipoles. Partial compensation takes place in the aqueous phase when the potential is measured through air ionised by a radioactive source; this also occurs when the interface is completely polarisable because the air has practically no ions in it. The rôle of the ionised air particles is that of mere current carriers for the measuring apparatus and they are swept into the aqueous phase.

The authors would like to express their thanks to Professor E. K. Rideal, F.R.S., and Dr. J. H. Schulman for their constant help, advice, and encouragement throughout the course of this work.

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## PART II.—(C) COLLOID STABILITY.

### THE ROLE OF THE FORCES BETWEEN THE PARTICLES IN ELECTRODEPOSITION AND OTHER PHENOMENA.

By H. C. HAMAKER AND E. J. W. VERWEY.

*Received 28th October, 1939.*

#### 1. Introduction.

The consequences of the assumption that the forces between colloidal particles result from the superposition of a repulsion and an attraction which vary with the composition of the sol have been analysed by one of the authors <sup>1, 2, 3, 4</sup> in previous papers.

It would seem appropriate to bring these principles under discussion at this meeting, but it would, on the other hand, be unsatisfactory to expound again what has already been explained elsewhere. We will therefore discuss a practical application which has actually been the starting point of our theoretical investigations, hoping, however, that you will feel at liberty to comment the earlier papers as well.

#### 2. Electrodeposition from Lyophobic Suspensions.

If we apply a voltage of 50 to 100 v. to electrodes immersed in a suspension of bariumcarbonate in ethanol it is observed that under suitable conditions the cathode is rapidly coated with a layer of the suspended material.<sup>5</sup> The experimental features of this phenomenon will be discussed in the section on "Technical Applications." Insight, however, into what are the conditions required for the formation of such a layer was not derived from the detailed experiments but from some observations concerning the general behaviour of our suspensions. These will briefly be considered here. Details will be given in a paper by the second author to appear in the *Rec. Trav. Chim. des Pays-Bas*, where the general colloid chemical aspects and the stability conditions of these suspensions in organic media will be discussed.

(1) As with colloidal solutions we may distinguish between stable and flocculating suspensions. In a stable suspension the particles though they may rapidly settle show no tendency to cluster together as long as they have not reached the bottom of the vessel. In a flocculating suspension, which may be prepared from a stable one by adding electrolytes or by a change in the dispersion medium, the particles

<sup>1</sup> H. C. Hamaker, *Rec. trav. chim.*, 1936, **55**, 1015.

<sup>2</sup> *Ibid.*, 1937, **56**, 3.

<sup>3</sup> *Ibid.*, 727.

<sup>4</sup> *Ibid.*, *Hydrophobic Colloids*; D. B. Centen, Amsterdam, 1937, pp. 16-46.

<sup>5</sup> J. H. de Boer, H. C. Hamaker and E. J. W. Verwey, *Rec. trav. chim.*, 1939, **58**, 662.

cluster together to large flakes from which the sediment is afterwards built up.

Now it was found that for the formation of a deposit by electrophoresis it is as a rule necessary to use stable suspensions. Though in a coagulating suspension the particles will still move towards one of the electrodes they are not deposited on it.

(2) If left standing for some time the stable suspensions which give a satisfactory electrodeposit are observed to produce a sediment which strongly adheres to the bottom of the vessel, so that prolonged shaking is often required to redisperse the material. Flocculating suspensions give a sediment of much lower density and without any marked mechanical strength.

From these observations we conclude that the parallelism between the formation of an adherent layer by sedimentation and by electrophoresis is not merely accidental but that these two phenomena are identical in nature. If so, the electric charges on the particles do not play an essential part in the formation of an electrophoretic deposit; the chief action of the electric field consists in moving the particles towards the electrode and in producing a force which presses the particles together on the surface of the electrode in the same way as the force of gravity presses them on the bottom.

Once this view is adopted we may simplify matters by neglecting for the moment the electric side of the phenomenon restricting our investigation to the formation of a deposit by sedimentation. This is a purely mechanical problem.

The stability of the suspensions used leads to the conclusion that at some distance from each other the forces between the particles must be repulsive, so that plotting the energy of interaction of two particles as a function of the distance between them (potential curve) we may have either a curve of type (a) in Fig. 1 or a curve of type (b).<sup>1, 3, 4</sup> At first sight it may be thought that only a curve of type (b) can lead to an adhesive deposit, the energy minimum *F* explaining the mutual adhesion between the particles when in touch with each other. Several observations indicate, however, that even when the forces between the particles are everywhere repulsive (curve (a) in Fig. 1) it is still conceivable that a strongly adhering deposit is obtained when the particles are sufficiently pressed together.

From our experimental data we have as yet been unable to decide whether one of these cases (curve (a) or curve (b)) is of more common occurrence than the other; it seems likely that they are both encountered in practical cases and we will therefore investigate the mechanism of the formation of a deposit in both instances.

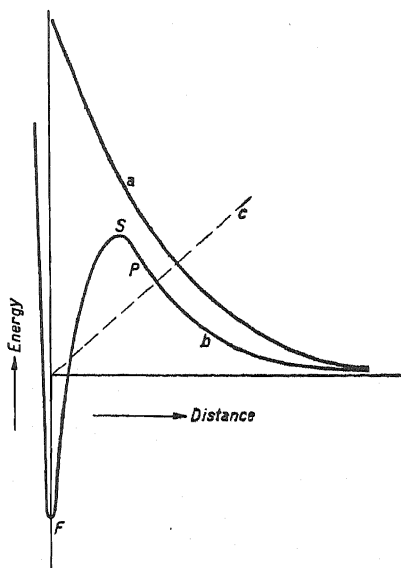


FIG. 1.—Two different types of potential curves which may explain the formation of a deposit.



### 3. Theory of the Formation of a Deposit.

We will begin by considering curve (b) in Fig. 1, in which case the phenomena are slightly more complicated. Once this case has been fully analysed the conditions prevailing when curve (a) holds are easily understood.

In connection with curve (b) (Fig. 1) two questions must now be answered, viz. :—

(1) How the formation of an adhering deposit takes place notwithstanding the existence of a stabilising maximum S in the potential curve.

(2) Why this maximum S should be an essential condition for the formation of a deposit.

The energy required to separate two particles in contact will, in Fig. 1, be given by the difference between the maximum S and the minimum F. It must be emphasised, however, that this energy is not the chief factor which determines the mechanical strength of the layer ;

for it is easily understood that the homogeneity of the distribution of the particles in the deposit will have a much more pronounced influence.

In the sediment of a flocculating suspension the flakes from which the bottom deposit is piled up will touch each other at a few points only ; the internal structure of the sediment will consequently be highly irregular so that there are numerous weak points where the layer breaks up upon a small disturbance.

On the other hand, in a stable suspension the particles will settle separately ; the particles which first arrive will not at once reach the very bottom, but they will

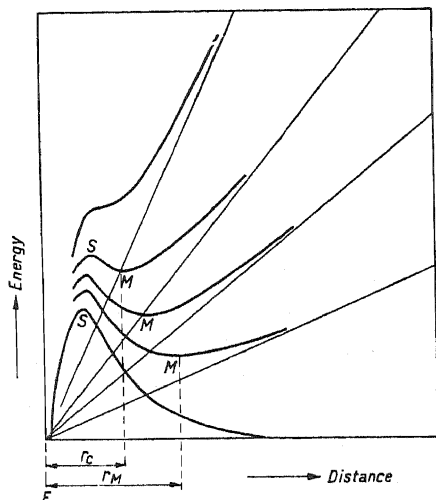


FIG. 2.—The process of deposit formation depicted in the case of curve (b) in Fig. 1.

float above the bottom at a distance at which their weight is balanced by the repulsive forces prevailing at large distances. But gradually when more particles settle the higher particles will come to press by their weight on the lower particles, which will be more and more forced together. The pressure which thus arises can be schematised in Fig. 1 by a straight curve through the origin, the slope of this curve increasing with the pressure. Under these circumstances the situation is no longer depicted by curve (b) in Fig. 1, but will be represented by the sum of curves (b) and (c). In Fig. 2 a set of resultant curves for increasing values of the pressure have been drawn.

The average distance between the particles in a suspension subject to these conditions will evidently be the distance  $r_M$  at which the minimum M occurs. But we see that when the pressure increases the difference between the maximum S and the minimum M gradually reduces and finally both S and M disappear. Before this stage is reached the difference S—M will become so small that by thermal agitation the

particles one after the other will be pushed from M over S and drop into the energy minimum at F; that is, they are withdrawn from the suspension and deposited in the layer.

The essential feature of these processes is that near the bottom the concentration is first increased as much as possible, the suspension being all the time a stable one with a homogeneous distribution of the particles. Finally, from a highly concentrated suspension the particles are systematically deposited in the layer, the issue being necessarily a deposit of a much more homogeneous structure and consequently of greater mechanical strength than is obtained from a coagulating suspension.

The number of particles which are deposited per second will depend on the difference between the minimum M and the maximum S and consequently (see Fig. 2) on the pressure. A stationary state will be reached when the number of particles added per second to the deposit is equal to the number transported towards the bottom by sedimentation.

This, however, does not hold during electrodeposition, for the conditions are slightly more complicated in that case, as is illustrated in Fig. 4a. In this figure we have plotted the concentration in the suspension when layer formation is going on.

Starting at the electrode A we first pass the layer already deposited which has been indicated as a region of high but constant concentration. At the surface B, where the actual formation of the deposit is going on, the concentration discontinuously decreases corresponding to the transition from the layer to the concentrated suspension. Next from B to C the concentration gradually decreases; the surplus of particles between B and C cause the pressure requisite for the formation of a deposit at B. From C to D the suspension has its normal concentration, and finally from D to E we pass a zone which has been deprived of its particles by the electrophoretic transport towards A.

The conditions depicted in Fig. 4a, however, are not stable; for the high concentration in the region B—C and the low concentration prevailing from D to E will necessarily give rise to convection currents, *a.o.* to a descending current between B and C. By this convection current a part of the particles transported towards A will be carried downwards being thus no longer available for the formation of a deposit. In our experiments these processes were manifest from an accumulation of suspended material on the bottom of the vessel underneath the electrode coated. Evidently only a part of the particles moving towards A are actually deposited on this electrode. This phenomenon is entirely comparable with Pauli's electrodecentration.<sup>6</sup> Some further consequences of Fig. 4 will be considered when dealing with our experiments.

Let us now return to Fig. 2. Layer formation as explained consists in the discontinuous transition from a concentrated suspension in which the average distance between the particles has a certain critical value (for instance  $r_c$  in Fig. 2) into a layer in which the particles touch;  $r_c$  is the distance at which the minimum M occurs when the difference between S and M becomes of the same order as the kinetic energy of the Brownian motion.

Evidently the smaller the critical distance  $r_c$  the more regular will be the structure of the deposit and the greater its mechanical stability. By constructing sets of curves as drawn in Fig. 2 it is easily found that

<sup>6</sup> Wo. Pauli, *Naturwiss.*, 1932, **30**, 555; E. J. W. Verwey and H. R. Kruyt *Z. physik. Chem.*, A, 1933, **167**, 151.

the critical value  $r_c$  will depend on the height of the maximum S, but also and more markedly on the distance at which the maximum slope in the potential curve (point P in Fig. 1) occurs.

As has been explained elsewhere<sup>1, 4</sup> the curve of Fig. 1 results from the superposition of a repulsion and an attraction, the former being undoubtedly due to the electric charges. Hence we may expect a relation between the  $\zeta$  potential and the formation of an adhering deposit as has been observed by one of us (V), a high  $\zeta$  being especially favourable for electrodeposition.

It is possible, however, that the ionic strength of the dispersive fluid is another factor which must be taken into account.

Now that we have fully dealt with the case of curve (b) in Fig. 1, we will proceed to discuss deposit formation when curve (a) is valid. In this instance, too, the particles settling on the bottom of the electrode

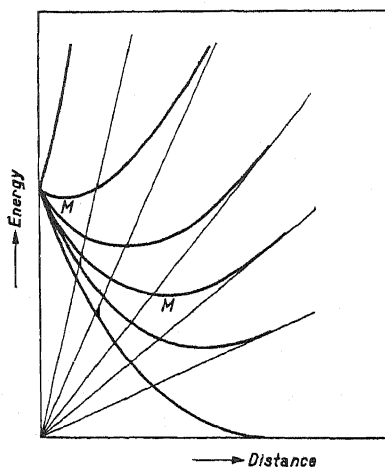


FIG. 3.—Deposit formation when curve (a) in Fig. 1 holds.

are gradually pressed together forming all the time a stable suspension with a homogeneous distribution of its particles. Ultimately a stop is put to this process when the particles come in touch with one another; the outcome is a layer of very dense structure and the frictional forces between the particles in contact will suffice to give this layer a high mechanical rigidity. These processes are illustrated by the set of curves given in Fig. 3, which being the counterpart of Fig. 2 requires no further explanation.

If, for instance, by switching off the electric current in the case of electrophoresis the force on the particles is stopped, the deposit will tend to expand into a stable suspension. This expansion, however, implies a flow

in the layer which may be greatly inhibited by the frictional forces between the particles; hence it will be a slow diffusion process, so that even in the absence of a compressive force the mechanical strength of the layer may continue to exist over a long period. Besides by a slight recrystallisation at the points of contact the layer may sinter together into a perfectly rigid structure, a possibility which is never entirely excluded. If so, a transition backwards to a stable suspension will not be observed at all.

Likewise if we try to redisperse the deposit by shaking, it will only be possible to remove the uppermost layer of particles at a time, so that long and vigorous shaking may be required before the entire deposit is destructed in that way.

A strong argument in favour of deposit formation under the conditions of curve (a) in Fig. 1 is furnished by the experimental fact that suspensions showing the phenomenon of dilatancy when sufficiently concentrated give very satisfactory sediments when subjected to electrophoresis. According to the present conceptions<sup>7</sup> the phenomenon of

<sup>7</sup> E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.*, 1938, **57**, 383; H. Freundlich and H. L. Röder, *Trans. Faraday Soc.*, 1938, **34**, 308.

dilatancy must be explained by a pure repulsion between the particles as represented by curve (a) in Fig. 1.

In this connection it may also be noted that we sometimes obtained electrophoretic layers which behaved like highly viscous fluids, so that they would flow off from the electrode when they were prevented from drying. We should hesitate, however, to interpret this as a definite proof that curve (a) holds. For with curves of type (b) it is quite conceivable that occasionally we obtain layers of somewhat irregular structure which are no longer capable of supporting their own weight and consequently exhibit a certain fluidity.

It is hardly necessary to mention that when curve (a) holds there will not be a jump in the concentration as drawn in Fig. 4a, but the

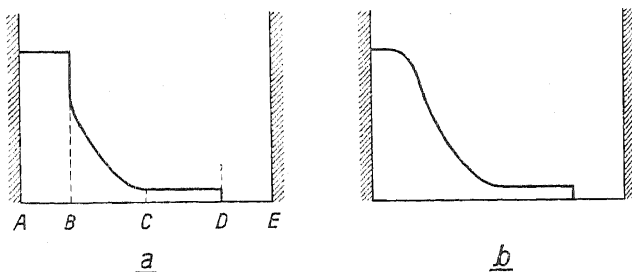


FIG. 4.—The concentration in the suspension during electrophoretic deposition.

transition from the layer to the suspension will be perfectly continuous as indicated in Fig. 4b.

From all this we conclude that the formation of a deposit can just as well be explained by curve (a) as by curve (b) in Fig. 1. The layers obtained should exhibit slightly different properties, but these differences are not sufficiently pronounced to distinguish between the two types of potential curves in an unambiguous way; partly this is also due to various complications which can never entirely be neglected. From extensive systematic observations it should be possible, however, to arrive at more definite conclusions, a point which will be considered in the following paper.

In conclusion, the authors wish to express their indebtedness to Dr. J. H. de Boer for stimulating discussions.

### Summary.

In studying the formation of a deposit by electrophoresis from suspensions in organic media a general parallelism was observed between electrodeposition and the formation of a sediment by gravity. This suggests that electrodeposition is mainly a mechanical problem, the electric nature of the phenomena being of secondary importance; the role of the electric field is only to provide a force which moves the particles towards and presses them together on the electrode.

Starting from this point of view the process of deposit formation is analysed by using potential curves. Two different types of curves are found capable of explaining the phenomena. The formation of a deposit in these two cases is discussed in detail. They should lead to slightly different properties of the layer but in the case of suspensions at least the differences are not sufficiently pronounced to discriminate between the theoretical possibilities.

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# THE INFLUENCE OF PARTICLE SIZE ON THE PHYSICAL BEHAVIOUR OF COLLOIDAL SYSTEMS.

By H. C. HAMAKER.

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## 1. Introduction.

In the foregoing paper<sup>1</sup> we have discussed the formation of a deposit from a suspension by sedimentation or by electrophoresis. The theories advanced can easily be extended so that they will apply to colloidal systems in general. We are thereby led to a more systematic study of the behaviour of a colloid under the force of gravity or under centrifugal forces, problems which will form the main topic of the following discussions.

It is generally accepted and it has been repeatedly enunciated that the difference between suspensions and colloidal solutions is only a difference in particle size and not a difference in the nature of the forces that are at work. Even from this point of view, however, the size of the particles will be a very important factor. For such phenomena, as we discussed in the paper mentioned, do not depend on the magnitude of a single force, but on the ratio of forces of different origin; and as each of these forces will vary in its own way the ratio between them may be considerably influenced by the size of the particles. First of all, this point will merit a closer examination.

## 2. The Influence of the Size of the Particles on the Process Acting upon them.

The forces to be considered are :—

- (1) The mutual forces between the particles,
- (2) the force of gravity and centrifugal forces,
- (3) the force exerted by an electric field,
- (4) forces due to friction or inertia (when we try to peptise a deposit by shaking).

Let us now investigate how these forces change with particle size.

Gravitational and centrifugal forces vary with the mass of the particles and therefore with the third power of particle radius ( $r^3$ ), and the same will hold with respect to the inertia forces mentioned under (4). It will be noted that centrifugal forces have not yet played a part in our previous arguments, but these have been added in view of the discussions which follow in § 3.

The frictional forces exerted by the agitated fluid on the particles in the deposit will be proportional to the surface and consequently vary with  $r^2$ .

<sup>1</sup> H. C. Hamaker and E. J. W. Verwey, *This volume*, page 180. This paper will be cited as (I).

For a particle in electrophoretic motion the electric force is balanced by the friction exerted by the fluid. We have in fact by Stokes law

$$F = 6 \cdot \pi \cdot \eta \cdot r \cdot v \quad (1)$$

and by the Helmholtz equation

$$v = \frac{\epsilon \cdot E \cdot \zeta}{6 \cdot \pi \cdot \eta} \quad (2)$$

and hence

$$F = \epsilon \cdot E \cdot \zeta \cdot r \quad (3)$$

where  $F$  is the force,  $v$  the electrophoretic velocity,  $\eta$  the viscosity,  $\epsilon$  the dielectric constant,  $E$  the electric field and  $\zeta$  the  $\zeta$  potential,  $r$  being the particle radius as before. We see that the force produced by an electric field varies as the first power of the particle size, since we know that  $\zeta$  varies but little with  $r$ .

From equation (3) the magnitude of the electric force is readily estimated. For instance for  $\zeta = 100$  mV  $= 3.33 \times 10^{-4}$  e.s.u. and  $E = 1$  V/cm.  $= 3.33 \times 10^{-3}$  e.s.u., and  $2r = 1\mu = 10^{-4}$  cm. we obtain with  $\epsilon = 30$  (methanol)

$$F = 1.7 \times 10^{-9} \text{ dyne} = \pm 2 \times 10^{-12} \text{ g.}$$

Thus for particles  $1\mu$  in diameter the force exerted by a field of 1 V/cm. is of the same order as the particle weight. In our electrophoretic experiments the field was of the order<sup>2</sup> of 100 to 500 V/cm., so that the action of the electric field was many times stronger than that of gravitation.

As has been explained in earlier papers<sup>3</sup> the influence of electrolytes can generally be depicted by a set of potential curves as drawn in Fig. 1. An increase in electrolyte content corresponds to a shift in the direction from curve 1 to curve 7. It would be of interest to know whether, *coeteris paribus*, we have also to expect a change in the type of the potential curve with a change in the size of the particles, but as yet it seems impossible to settle this point.

Calculations<sup>4</sup> show that for spherical particles the London —v. d. Waals' attraction varies as the first power of particle size. If, however, the

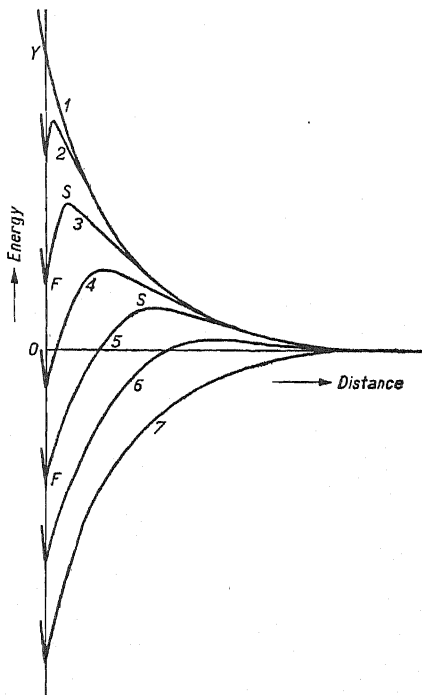


FIG. 1.—Set of potential curves representing the changes in a hydrophobic colloid caused by changes in the concentration of electrolytes.

<sup>2</sup> This volume, page 279.

<sup>3</sup> H. C. Hamaker, *Rec. trav. chim.*, 1936, 55, 1015; 1937, 56, 3, 727; *Hydrophobic Colloids*, D. B. Centen, Amsterdam, 1937, pp. 16-46.

<sup>4</sup> H. C. Hamaker, *Physica*, 1937, 4, 1058.

particles are of irregular shape they will approach one another at a few points only and the energy of interaction will mainly be concentrated in the neighbourhood of these contact points. In that case we should expect the forces to vary even less with the size of the particles.

Furthermore, elementary observations show that stability and coagulation occur in suspensions at about the same electrolyte concentrations at which they are observed in true colloidal solutions. If we attribute coagulation to London—v. d. Waals' attraction we may draw the conclusion that the electric forces vary in the same way with the size of the particles as these attractive forces. We should therefore in general expect the forces between the particles to vary with something between the zeroth and first power of the particle radius.

Recently Levine<sup>5</sup> and Levine and Dube<sup>6, 7</sup> have carried out more precise calculations of the electric interaction of colloidal particles. According to their results electric forces alone should produce an energy minimum at a given distance. In Fig. 6 of the first paper<sup>5</sup> the value of this minimum has been plotted as a function of the electrolyte concentration for particles with a radius  $10^{-6}$  cm. and a charge  $Q = 100e$ . Using the relation

$$\zeta = \frac{Q}{Da(1 + \kappa a)}$$

we may from this curve derive a second one giving the minimum energy as a function of particle radius  $r$  for fixed values of the  $\zeta$  potential and the electrolyte concentration. For  $\zeta = 100$  mV. and  $\gamma = 1$  mMol./l.

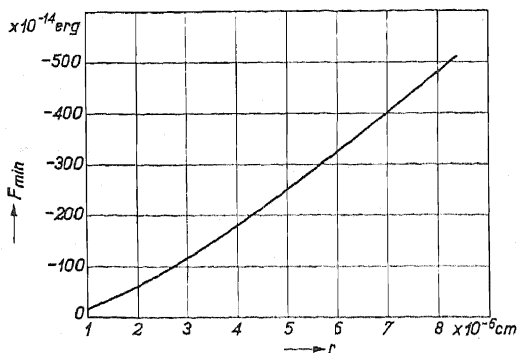


FIG. 2.—Value of Levine's energy minimum as a function of particle radius for  $\xi = 100$  mV.,  $\gamma = 1$  mMol./l.

alone would cause coagulation so that under these normal conditions a suspension could not be stable at all. Since this is at variance with experiment some important factor must have been omitted and we can not apply Levine's results with confidence in settling our present problem.

Fig. 2 refers to metallic particles, but Figs. 2 and 3 in the third paper<sup>7</sup> demonstrates that for insulating particles the energy minimum

the result is plotted in Fig. 2. The value of the minimum increases approximately in the same proportion as the size of the particles, soon reaching values of more than  $400 \times 10^{-14}$  erg or  $100 kT$ . Besides this minimum occurs when the particles are comparatively close together, say about  $1/10$  of a particle radius apart. Hence the electric forces

<sup>5</sup> S. Levine, *Proc. Roy. Soc., A*, 1939, **170**, 145-182.

<sup>6</sup> S. Levine and G. P. Dube, *Trans. Faraday Soc.*, 1939, **35**, 1125.

<sup>7</sup> G. P. Dube and S. Levine, *ibid.*, 1939, **35**, 1141.

is still more pronounced so that our objections will hold in that case as well.

### 3. Sedimentation and Deposit Formation in Colloidal Systems in General.

By the principles set forth in the last section we may now extend the theories of (I) to colloidal systems in general. Thereby we shall, on the one hand, be led to discuss phenomena with which we are long since acquainted, but, on the other hand, our theories suggest a novel method of experimenting with colloidal solutions. We have not carried out any experiments of this kind, but we give our conclusions in the hope that they may serve as a guide in an interesting and as yet untouched field of research.

Let us begin by considering cases in which a potential curve of type 1 in Fig. 1 is valid. When the particles are large enough the suspension settles by gravity forming a sediment as described in (I). But if the size of the particles is reduced the particle weight ( $r^3$ ) diminishes much more rapidly than the repulsive forces ( $r^0$  to  $r^1$ ); hence we shall ultimately reach a state in which the influence of gravity is hardly perceptible and the particles will remain homogeneously distributed for any length of time. This is, of course, also partly due to the greater importance of Brownian motion in systems with small particles, but as Levine<sup>8</sup> has shown the homogeneous state persisting in many colloidal solutions mainly results from the repulsive forces between the particles.

But sedimentation, when it is no longer produced by the force of gravity alone, can still be brought about in a centrifuge. We should then even be in a position to apply a centrifugal force of any desired strength during a given period and afterwards observe the properties of the sediment when the force is stopped. We should in that case expect to observe the following phenomena.

Moderate centrifuging will produce a concentrated sol near the bottom of the vessel which by its greater density will behave as a separate fluid but which is readily redispersed by shaking. If we increase the speed of the centrifuge this concentrated sol will gradually pass over into a solid deposit which can be re-precipitated by shaking though this may now be a slow process. If left to itself after centrifuging the system should under all circumstances diffuse back into the original homogeneous state.

One restriction must here be made, however. Frequently colloidal particles when brought in touch with one another will sinter together by a slight re-crystallisation at the contact points, which would render phenomena irreversible which should, from a theoretical point of view, be reversible. This cementing together is in fact the chief process by which unfilterable precipitates are rendered filterable in the course of time.<sup>9</sup> To avoid these ageing phenomena we should preferably use colloids which can readily be re-precipitated by washing even if they existed in the coagulated state for a considerable time.

Since the forces exerted on the particles by an electric field vary in the same way as the forces acting between the particles the formation

<sup>8</sup> S. Levine, *Proc. Roy. Soc., A*, 1934, 146, 597.

<sup>9</sup> H. M. Trimble, *J. Physic. Chem.*, 1927, 31, 601; I. M. Kolthoff, *J. Physic. Chem.*, 1932, 36, 860.



of a deposit by electrophoresis will not be greatly influenced by the size of the particles. But if the electric field is reduced it will finally become too weak to produce a deposit at all. The particles are then merely concentrated near one of the electrodes from where the concentrated sol will sink to the bottom by its high density (Electrodecantation).

From curve 1 in Fig. 1 we pass to curve 3 or 4 by adding a certain amount of electrolytes. The formation of a deposit under these altered conditions has been described *in extenso* in (I). In contrast with curve 1 the deposit should not diffuse backwards into a stable colloid when centrifuging is stopped.

We generally observed that a sediment obtained from a stable suspension can be re-peptised by shaking. That this will be the case when curve 1 in Fig. 1 holds is evident, but whether it will also be true when curves 3 or 4 are valid is a point which requires a more detailed analysis. The energy difference between the maximum  $S$  and the minimum  $F$  in these potential curves must be of the order of several times  $kT$  or, say, about  $10^{-12}$  erg. If this energy is to be supplied over a distance of  $10^{-6}$  cm. the requisite force will amount to  $10^{-6}$  dyne or  $\pm 10^{-9}$  g., which for particles  $1\mu$  in size is about 300 times the particle weight. Whether it is actually possible to apply forces of this order of magnitude by shaking is in itself open to question, though it is not excluded. Since, however, the frictional and inertia forces exerted by shaking will decrease much more rapidly with particle size than the adhesive forces between the particles, a re-peptisation by shaking, if possible at all, will be observed only in systems with large particles but is quite excluded in true colloidal solutions.

Hence, from a colloid in which curves 3 or 4 holds, we should, when the speed of the centrifuge surpasses a certain limit, obtain a deposit which can not be re-peptised by shaking. But under suitable conditions a redispersion will be possible by washing the sediment with a fluid of lower electrolyte content (transition to curve 1). A similar conclusion will, of course, pertain to the deposit prepared by electrophoresis.

It will now be clear how by systematic observations we may distinguish between the different types of potential curves presented in Fig. 1. Such investigations would furnish the most straightforward evidence in favour of the theories based on these potential curves.

It will be noted that our theory is only a very schematic one. The irregular shape of the particles, for one thing, has been disregarded, a factor which may soon lead to complications when more detailed observations are carried out. Furthermore, the use of potential curves implies that we consider the behaviour of two particles with respect to one another as representative of the behaviour of the entire system. Whether this is allowable, for instance, in a close packed sediment is open to question; at present, however, this view seems to go a long way in explaining colloidal phenomena and there is little reason to abandon our standpoint until our theories are definitely contradicted by experiment.

#### 4. Literature.

The problems of colloid chemistry have never been approached from the point of view discussed in the present paper, so that in literature only a few occasional remarks are found which bear on our problems.

Freundlich<sup>10</sup> mentions as a general experience that lyophobic

<sup>10</sup> H. Freundlich, *Kapillarchemie*, II, 1932, p. 76.

colloids cannot as a rule be peptised anew after centrifuging. It is likely, however, that in the cases Freundlich had in mind this is chiefly due to ageing of the precipitate and has nothing to do with our potential curves.

The various degrees of sedimentation have been realised in the experiments designed to determine Avogadro's number. Amongst these Westgren,<sup>11</sup> for instance, mentions that a gold sol is by moderate centrifuging concentrated to a heavy fluid on the bottom which is readily redispersed by shaking. However, he does not mention what happens at a higher speed of the centrifuge.

Extensive observations on the sediment volume of suspensions were carried out by v. Buzagh<sup>12</sup> and by Ostwald and Haller.<sup>13</sup> These investigations were chiefly made, however, with coagulating suspensions, from which we get sediments without any adhesive properties.

In a variety of fluids v. Buzagh observed for quartz a general parallelism between the sediment volume and the adhesive forces, measured by the angle at which the quartz particles start to slide down a sloping quartz plate; a strong adhesion corresponds to a voluminous sediment. This is indeed what we should expect. The volume of a sediment piled up of flakes will greatly depend on the degree of deformation of these flakes under the weight of the layers above them; greater adhesion will occasion a greater resistance against deformation and consequently a larger volume. V. Buzagh interprets his results preferably in terms of a lyosphere surrounding the particles and he almost completely disregards the influence of the electric repulsion which should have very much the same influence. As a matter of fact the concept of a lyosphere is introduced to represent a repulsive action between the particles other than that resulting from the electric charges. We should, however, have recourse to this idea only when it is definitely ascertained that the electric forces fail to explain the observations.

Ostwald and Haller established a close correspondence between the dielectric constant of the dispersion fluid and the density of the sediment, a large  $\epsilon$  giving a small sediment volume. It is quite conceivable that this is again indirectly a consequence of the electric forces; for a high dielectric constant generally goes together with a strong electrolytic dissociative power and therefore with a well-developed double layer. Ostwald and Haller's view that the changes in the sediment volume should be entirely attributable to the thickness of the lyospheres around each individual particles seems quite untenable.

Ehrenberg<sup>14</sup> and after him, v. Buzagh,<sup>12</sup> have drawn attention to the differences in sediment volumes between stable and coagulating suspensions, which they explained in the same sense as we have done. No attention has so far been paid, however, to the remarkable adhesion of the sediment of a stable system whereas this phenomenon has been the main starting-point for the considerations presented in this and the foregoing paper.

In conclusion, the author wishes to express his thanks to Dr. E. J. W. Verwey for valuable advice.

<sup>11</sup> A. Westgren, *Z. anorg. Chem.*, 1915, **93**, 231.

<sup>12</sup> A. v. Buzagh, *Koll. Beihefte*, 1931, **32**, 114.

<sup>13</sup> W. Ostwald and W. Haller, *ibid.*, 1929, **29**, 354.

<sup>14</sup> Ehrenberg, *Bodenkolloide*, pp. 83 ff., Fresden, 1918.

### Summary.

It is generally assumed that the difference between suspensions and colloidal solutions is only a difference in particle size. Even then, however, the size of the particles will be a very important factor. For many properties of a sol depend on the ratio of forces of different origin which act on the particles. Each of these forces will vary in its own way so that their ratios may greatly be influenced by particle size.

In § 2 the various forces which may play a part and their dependence on particle size is discussed. On the basis of this analysis the behaviour of colloidal systems under gravity or in a centrifuge is discussed in § 3. It is specially suggested that observations on the properties of a deposit obtained by centrifuging may provide valuable information concerning the shape of the potential curves valid in the sol.

Literature dealing with similar problems is discussed in the last section.

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## ELECTRICAL DOUBLE LAYER AND STABILITY OF EMULSIONS.

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### 1. Origin and Order of Magnitude of the Double Layer Potential.

For a system of two immiscible liquids in mutual contact the potential difference between the interior of the liquids is determined by a distribution equilibrium of the ions present in the system; each electrolyte, distributed about two phases, acts as a potential-determining electrolyte<sup>1</sup>, even when the solubility in one of the phases is extremely small<sup>2</sup>.

These electrolytes may have been added deliberately to the system; in the other case the liquids used generally contain sufficient electrolytic impurities to build up a double layer at the interface ( $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$  ions in water, organic acids in organic liquids, etc.). This electrical double layer is a direct consequence of the generally unequal distribution coefficient of the positive and negative ions. In the bulk liquid phases there are no space charges and the ionic concentrations are constant. In the neighbourhood of the interface the ionic concentration of one sign increases and that of the other sign decreases in such a way that the total charge on both sides of the interface is equal but has opposite signs (double layer with two "diffuse" layers).

Our considerations are restricted to those cases where equilibrium conditions have been reached and this double layer has been established.

<sup>1</sup> R. Beutner, *Die Erzeugung galvanischer Ströme im lebenden Gewebe*, 1920. H. Freundlich and A. Gyemant, *Z. physik. Chem.*, 1922, **100**, 182. N. Bjerrum and E. Larsson, *Z. physik. Chem.*, 1927, **127**, 358. I. M. Kolthoff, *Chem. Weekbl.*, 1937, **34**, 785. G. C. H. Ehrensvärd and L. G. Sillen, *Z. Elektrochem.*, 1939, **45**, 440. E. J. W. Verwey and K. F. Niessen, *Phil. Mag.* (in the press).

<sup>2</sup> Cf. also M. Coehn and R. Raydt, *Ann. Physik.*, 1909, **30**, 777.

In some of the investigations concerning the electrical phenomena at oil-water interfaces these conditions were probably not realized.

The thermodynamical relations have already been discussed by Nernst, van Laar and others; by considering that the free energy  $e\phi + \mu + kT \log c$  for each ion is identical in both phases, we find for the distribution coefficient of a 1-1 valent electrolyte and the corresponding potential difference:

$$2kT \ln \frac{c_1}{c_2} = (\mu_2^+ - \mu_1^+) + (\mu_2^- - \mu_1^-) \quad (1)$$

$$2e(\phi_1 - \phi_2) = (\mu_2^+ - \mu_1^+) - (\mu_2^- - \mu_1^-) \quad (2)$$

where  $\phi_1$  is the potential in the interior of phase 1,  $\phi_2$  that in phase 2,  $\mu_1^+$  the chemical potential of the cation (for instance in the standard state) in phase 1, etc., and  $c_1$  and  $c_2$  are the ionic concentrations.

Since it is assumed that the free energy varies with the concentration in both phases according to the term  $kT \ln c$  (diluted solutions), and we only have to consider differences of the thermodynamical potential ( $\mu_2^+ - \mu_1^+$  and  $\mu_2^- - \mu_1^-$ ) we may take, for  $\mu_1^+$ , etc., the molal free energies for infinitely diluted solutions.

A fairly rough estimation of this free energy change accompanying the transition of an ion from the vacuum to the interior of the liquid phase is obtained by Born's equation:

$$\mu = -\frac{e^2}{2r} \left( 1 - \frac{1}{\epsilon} \right);$$

this equation considers only the electrical work, under the assumption that the ion is a rigid sphere with the charge  $e$  and the radius  $r$ , and the surrounding liquid a continuum with dielectric constant  $\epsilon$ . This simple equation has also been used by Rutgers<sup>3</sup> in a recent paper concerning the rule of Coehn and Raydt, but for a calculation of the internal energy and not for the free energy; this is certainly not correct since the field energy change given by Born's equation corresponds to an isothermal and reversible process and is therefore a free energy difference in the sense of thermodynamics<sup>4</sup>.

With the aid of this approximation of the  $\mu$ -values and assuming that  $r^+$  and  $r^-$  are independent of the solvent, the equations for  $c_1/c_2$  and  $\phi_1 - \phi_2$  are:

$$2.3 \cdot 10 \log \frac{c_1}{c_2} = \frac{e^2}{4kT} \cdot \frac{r^- + r^+}{r^+ r^-} \cdot \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 \epsilon_2} \quad (1')$$

$$\phi_1 - \phi_2 = \frac{e}{4} \cdot \frac{r^- - r^+}{r^+ r^-} \cdot \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 \epsilon_2} \quad (2')$$

It is generally overlooked that  $\phi_1 - \phi_2$  is not identical with  $D$ , the double layer potential. We must write:

$$\phi_1 - \phi_2 = \chi_{12} + D,$$

showing that the total potential difference between the internal of the phases is a superposition of the contact potential difference at the interface,  $\chi_{12}$ , due to oriented dipole-molecules and polarisation effects, and the double layer potential  $D$ . At the present moment we do not know anything about these  $\chi$ -potentials<sup>5</sup> at the interface of two liquids. For the free surface of water, i.e. at the interface water/vacuum, this boundary

<sup>3</sup> A. J. Rutgers, *Physica*, 1938, 5, 54.

<sup>4</sup> See, for instance, R. Becker, *Theorie der Elektrizität*, I, 10. Aufl. 1933, page 225.

<sup>5</sup> Terminology of E. Lange, cf. *Handb. Exp. Physik* XII, 2, 265-294 (1933).

potential drop (due to oriented  $\text{H}_2\text{O}$  molecules) is (after unpublished deductions by the author from measurements by E. Lange) about  $-0.5$  v. We cannot exclude the possibility that the  $\chi$ -potentials to be considered here are of the same order. As will be seen below,  $\phi_1 - \phi_2$  is generally of the order of  $0.1 - 0.3$  volts.  $\phi_1 - \phi_2$  and  $D$  are therefore far from identical and may even have opposite signs. Equation (2) shows that for  $r^- > r^+$  and  $\epsilon_1 > \epsilon_2$   $\phi_1 - \phi_2$  is positive; for the reasons mentioned above this does not necessarily imply that  $D$  is positive; we only can state that a positive value of  $D$  will be more probable. Hence equation (2) explains why the well-known rule of Coehn-Raydt holds in many cases; the negative charge of the phase with the smallest dielectric constant is a consequence of the fact that anions are generally larger than cations<sup>6</sup>; inversely, the rule of Coehn and Raydt is another indication that the potential difference at the interface of most two-liquid systems is caused by a distribution equilibrium of potential determining ions originating from small amounts of electrolytes which will always be present. Simultaneously, we see that this rule does not necessarily have general validity, even when  $r^- > r^+$ , since the distribution equilibrium of the electrolyte determines  $\phi_1 - \phi_2$  and not  $D$ .

Equations (1) and (1') can probably give a good estimate of the ionic concentrations; equations (2) and (2'), however, contain the difference of  $\mu_1$  and  $\mu_2$  for each ion, and must, therefore, be used carefully, since they entirely neglect specific influences of the solvents, which are not expressed by the dielectric constant and which could only be accounted for by a different (apparent) ionic radius in different solvents. Also for this reason we cannot draw many conclusions concerning the double layer potential with the aid of equation (2).

The ionic radii  $r^+$  and  $r^-$  stand for the distance from the centre of the ion to the centre of the dipole of an adjacent solvent molecule, and are therefore somewhat larger than the ionic radii in crystals.<sup>7</sup> They are of the order of  $2 \times 10^{-8}$  cm., so that  $\frac{r^+ + r^-}{r^+ r^-}$  will be about  $10^8$ . With this value we calculate for  $c_1/c_2$ , the ratio of the ionic concentrations, (which is not identical with the distribution coefficient of the electrolyte since in the phase with smallest dielectric constant also the degree of dissociation will be small) the values shown in Table I.

TABLE I.

$\epsilon_1$	$\epsilon_2$	$\text{Log } \frac{c_1}{c_2}$
80	5	12
80	10	5.5
80	15	3.4
80	20	2.3

TABLE I.

$\epsilon_1$	$\epsilon_2$	$\phi_1 - \phi_2$ (mV).
80	5	+ 180
80	10	+ 84
80	15	+ 52
80	20	+ 36

In the common case that  $r^- - r^+ = 10^{-8}$  cm., for instance

$$r^+ = 1.5 \times 10^{-8} \quad \text{and} \quad r^- = 2.5 \times 10^{-8},$$

we find for  $\phi_1 - \phi_2$  the values of Table II.

<sup>6</sup> E. J. W. Verwey, *Dissertation*, Utrecht 1934, page 61; A. J. Rutgers,<sup>3</sup>; cf. also *Hydrophobic Colloids*, pp. 55, 57, 62-64 (Symposium, Utrecht, 1937).

<sup>7</sup> Cf. A. Voet, *Trans. Far. Soc.*, 1936, **32**, 1301; W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. chem. physics*, 1939, **7**, 108.

In order to find  $D$  we ought to know  $\chi_{12}$ , but we may infer from the foregoing that  $|D|$  and  $|\phi_1 - \phi_2|$  are of the same order of magnitude, except in cases where one of the ions shows a strong specific tendency towards one of the phases, or where  $\chi_{12}$  (for  $\phi_1 - \phi_2$  positive) happens to be strongly negative, and therefore somewhat larger values of  $D$  may occur.

It is instructive to compare here the conditions at a liquid-liquid interface and those at a solid-liquid interface. In the case of Ag-I water (or, generally, if one of the phases is a solid) we can vary the concentration of the potential-determining ions and therefore their thermodynamical potential or free energy in the aqueous phase without a corresponding change in the solid. Thus the double layer potential of AgI in pure water (saturated with AgI,  $a_{I^-} = 10^{-8}$ ) is only  $-100$  mV.; but by raising the concentration of iodide ions to  $10^{-3}$  eq./l., the value of  $D$  can be made about  $300$  mV. more negative, *i.e.*  $D = -400$  mV. In the case of two liquids, however, an increase of the concentration of the electrolyte in one phase also rises that in the second, and  $\phi_1 - \phi_2$  and ( $\chi = \text{const.}$ )  $D$  is independent of the concentration (*cf.* equation (2')). Hence, in the latter case, we can freely choose the potential-determining electrolyte and thereby alter the double layer potential; once this choice has been made, however, we cannot change the potential by varying the concentration.

## 2. The Potential Function at the Liquid-liquid Interface and the Primary Stability of Emulsions.

We consider now the stability of emulsions, especially the *primary* stability<sup>8</sup> or peptisation conditions. By "stability" is meant the stability of the emulsion towards coagulation or sticking together of the liquid drops, not its stability in the thermodynamic sense.<sup>8</sup> We will exclude, for the time being, the case where a highly adsorbable ion is present in the system, and consider first the case where the potential-determining electrolytes are "normal" inactive electrolytes.

In that case there exists striking difference between the stability conditions of emulsions and those of suspensions and suspensoids (lyophobic colloids with solid particles). Many insoluble (or slightly soluble) solid substances can be peptised in liquids with a high dielectric constant, spontaneously or with the aid of small amounts of potential-determining electrolytes, whereas it is, under similar conditions, impossible to obtain stable emulsions. The very dilute oil-in-water hydrosols, obtained by pouring an alcoholic solution of the oil in water, are the only more or less stable emulsions known. Except these dilute emulsions, which are probably peptised by a capillary active impurity ion (*cf.* § 3), the preparation of an emulsion always requires the addition of special emulsifiers. Concentrated suspensions, but also concentrated suspensoid sols can easily be prepared, if only care is taken that during the preparation the concentration of the electrolyte is kept below the flocculating concentration (well known examples are the concentrated sols of Au, Fe<sub>2</sub>O<sub>3</sub>, AgI, the latter up to 50 %, obtained by electrode-decantation<sup>9</sup>). Emulsions cannot be obtained under these conditions.

<sup>8</sup> Cf. E. J. W. Verwey, *Chem. Rev.*, 1935, **16**, 388, 391.

<sup>9</sup> Wo. Pauli, *Naturw.*, 1932, **30**, 555. W. Neurath and Wo. Pauli, *Z. physik. Chem. (A)*, 1933, **163**, 351. E. J. W. Verwey and H. R. Kruyt, *ibid.*, 1933, **167**, 149.

The stability conditions of emulsions are fundamentally different from those of the lyophobic colloids.<sup>10</sup>

To understand this fundamental difference, we must investigate: (1) the  $\zeta$ -potential needed for stability under the conditions of preparation of these sols (critical  $\zeta$ -potential for primary stability), and (2) the nature of the electrical potential function in the double layer.

These questions, which are closely connected, will be considered first for the solid-liquid interface.

For glass in contact with water v. Smoluchowski<sup>11</sup> assumed that part of the potential drop in the double layer occurs in the solid phase. From investigations on the AgI-sol,<sup>12</sup> the present writer was brought to a similar assumption for AgI/water,<sup>13</sup>; a more close examination, however, led to a different conclusion. In the latter case the absolute value of the double layer potential could be determined, and in dialysed AgI-sols was found to be about  $-200$  mV. The  $\zeta$ -potential, however, calculated from the electrophoretic mobility with the aid of the Debye-equation, is only  $-60$  or  $-70$  mV.; from this it can be calculated that the potential drop in the aqueous layer is about  $-80$  mV. An explanation of the remaining  $-120$  mV., occurring within the AgI phase, has been given on the basis of discontinuity of the charges, but, as pointed out by de Bruyn, this explanation is incorrect, and it has therefore been suggested that the discrepancy between  $-80$  mV. and  $-200$  mV. is due to the insufficiency of Debye's equation, neglecting the relaxation effect.<sup>14</sup> The influence of these relaxation forces<sup>15</sup> for large values of  $\zeta$  ( $> 25$  mV.) has not yet been calculated for the present case, where the particle is small with respect to the thickness of the double layer, but applying the Debye-Hückel equations it can easily be shown that they will have a considerable effect. We will therefore, for the present, assume that in the case of a AgI-sol the whole potential drop  $D$  occurs in the aqueous phase. This accords with the view that the solid substance brought in contact with the solution phase will generally be incapable of taking up an excess of ions of one sign in the interior of the lattice, and therefore no space charge can be formed. In that case there is no possibility that part of the double layer potential drop occurs within the solid phase.

The absolute value of  $\zeta$  in dialysed AgI-sols is therefore only slightly smaller than  $200$  mV. We now want to know the critical  $\zeta$ -potential necessary for stabilisation. The theory of interaction of two lyophobic colloidal particles<sup>16</sup> is still insufficient to calculate this critical  $\zeta$ -potential in a given case, but it has taught us that this critical  $\zeta$ -potential depends on the properties of the medium and the nature of the electrolytes. Thus, the critical  $\zeta$ -potential for primary stability (where the experimental conditions are often such that the electrolyte concentration is low and the diffuse outer layer rather extensive) will be different from

<sup>10</sup> Cf. W. Clayton, *The Theory of Emulsions and their technical treatment*, 3rd. ed., London, 1935, pp. 5, 19, 80, 157. J. L. van der Minne, in *Hydrophobic Colloids*, Amsterdam, 1938, pp. 138, 145.

<sup>11</sup> M. v. Smoluchowski, *Graetz Handbuch der Elektriz.*, 1914, 2, 366.

<sup>12</sup> E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem. (A)*, 1934, 167, 149.

<sup>13</sup> E. J. W. Verwey, *Rec. trav. chim.*, 1934, 53, 933.

<sup>14</sup> H. de Bruyn, *Hydrophobic Colloids*, p. 79-80; E. J. W. Verwey, *ibid.*, p. 81-82.

<sup>15</sup> H. H. Paine, *Proc. Cambridge Phil. Soc.*, 1932, 28, 83. J. J. Bikerman, *Z. physik. Chem. (A)*, 1933, 163, 378. J. J. Hermans, *Phil. Mag. (7)*, 1938, 25, 426; 26, 650.

<sup>16</sup> H. C. Hamaker, *Rec. trav. chim.*, 1937, 56, 3. S. Levine, *Proc. Roy. Soc., A*, 1939, 170, 145. B. Derjaguin, *Acta Physico chimica U.R.S.S.*, 1939, 10, 333.

that for secondary stability (*i.e.*, in the case of flocculation with an electrolyte, where the concentration is much higher). In the case of AgI this critical  $\zeta$ -potential for primary stability can be determined roughly by titrating the dialysed negative sol with diluted  $\text{AgNO}_3$ , or the positive sol with a solution of KI. Flocculation occurs on both sides of the zero point of the charge when the concentration of the potential-determining ions ( $\text{Ag}^+$  or  $\text{I}^-$ ) differs from that at the zero point by a factor of about  $10^2$ , *i.e.*, the "critical" double layer potential is about

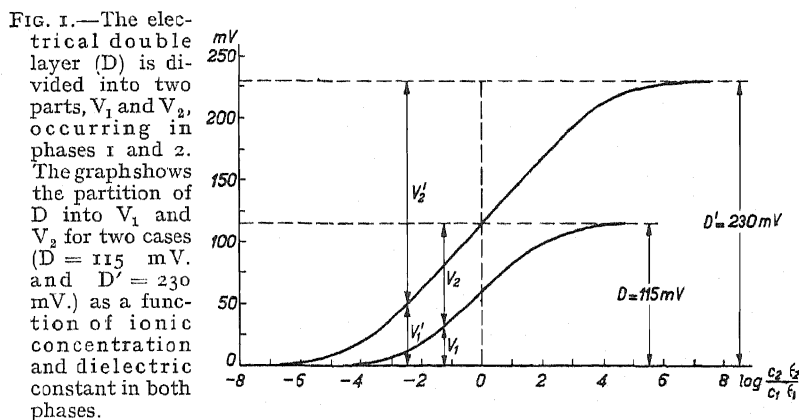
$$2 \times 58 = \pm 116 \text{ mV.},$$

and the "critical"  $\zeta$ -potential therefore about 100 mV.

It is reasonable to assume that for the stability of an oil-in-water emulsion, the potential drop in the outer sphere will be of the same order of magnitude as that for the stabilisation of AgI-sols (not exactly as, for instance, the van der Waals-London attraction forces will be different). In the case of a water-in-oil emulsion (or generally in the case that the dispersed particles have a lower dielectric constant and electrolyte concentration than the dispersion medium) we have no such experimental evidence from analogous suspensoid sols, but here the theory tells us at least qualitatively that, in this case, the critical  $\zeta$ -potential will be larger. We can, for instance, use the very approximate equation for the electrical repulsion at mutual contact of two spherical particles (radius  $a$ ):

$$F = \frac{E^2}{\kappa a} = \zeta^2 \kappa a \quad (3)$$

though this is only an approximation for small values of  $\zeta$  and  $\kappa a$  ( $E$  = particle charge,  $\epsilon$  = dielectric constant,  $\kappa^2 = \frac{8\pi e^2 n}{\epsilon kT}$  ( $a$  = radius of the particle)). In a medium with a lower dielectric constant the critical



$\zeta$ , being proportional to  $\epsilon^{-\frac{1}{2}}$ , is therefore larger than in a medium with a high dielectric constant. According to this estimation in a medium with  $\epsilon = 10$ , it will be of the order of 300 millivolts.

We now proceed to a consideration of the distribution of the electrical potential in the neighbourhood of a liquid-liquid interface. Going from one phase to the other, the potential falls off continuously on both sides of the interface because both phases are able to contain one of the ions



in excess. The double layer potential is therefore divided into two parts. In a previous paper<sup>1</sup> we have calculated this partition of the double layer potential ( $D$ ), for infinitely large phases and a flat interface. The result is plotted in Fig. 1, showing that the partial potential drops in phases 1 and 2 ( $V_1$  and  $V_2$ ) depend entirely on the numerical values of  $c_1/c_2$ ,  $\epsilon_1/\epsilon_2$  and  $D$  ( $c$  = ionic concentrations). If  $c_1\epsilon_1 > c_2\epsilon_2$ , we find  $V_1 < V_2$ , and inversely; especially for low values of  $D$  the partial potential drop in the phase with the largest dielectric constant (and, therefore, generally also the largest ionic concentration) becomes rather small as soon as  $c_1\epsilon_1$  differs considerably from  $c_2\epsilon_2$ .

The equations underlying Fig. 1 are no longer valid if the size of the drops of the emulsion or the average distance between the surfaces of

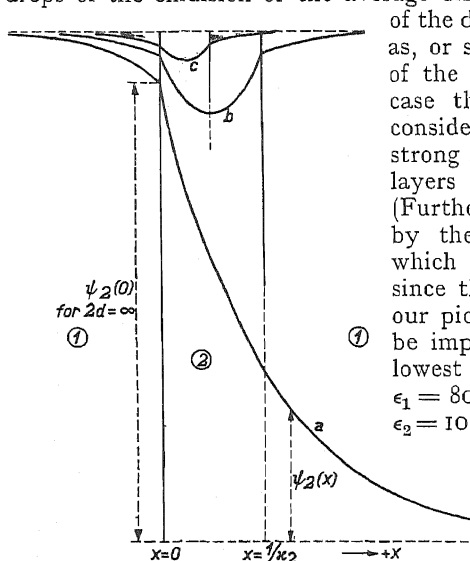


FIG. 2.—The interaction of two double layers. The electrical potential for small values of  $D$  in the case that the liquid with the smallest dielectric constant phase 2, is not infinitely large but present as a thin layer (thickness  $2d$ ) between two phases 1. Curve (a):  $2d = \infty$ ; curve (b):  $2d = 1/\kappa_2$ ; curve (c):  $2d = 1/2\kappa_2$ .

of the drops become of the same order as, or smaller than, the "thickness" of the diffuse layers ( $1/\kappa$ ). In that case the phases can no longer be considered as infinitely large and a strong interaction between the diffuse layers of adjacent interfaces occurs. (Further deviations will be introduced by the curvature of the interface which will not be considered here, since they do not essentially change our picture.) This interaction might be important in the phase with the lowest dielectric constant, where for  $\epsilon_1 = 80$ ,  $c_1 = 10^{-5}$  (equation 1) and  $\epsilon_2 = 10$ , according to equations (1) and (3),  $1/\kappa_2$  would be of the order  $10^{-3}$  cm. In the Appendix we have calculated the potential function for a thin liquid film of phase 2 (thickness  $2d$ ) between two infinitely large phases 1. If phase 2 is the phase with the lowest dielectric constant we find, for small values of  $D$ , potential curves as given in Fig. 2 for varying distances  $2d$  of

the interfaces. The result is independent of the numerical values of  $c$  and  $\kappa$  in both phases; in the drawing we have assumed  $c_1\epsilon_1 = 100$ ,  $c_2\epsilon_2$  and  $\kappa_1 = 2\kappa_2$ . It is seen that for small values of  $2d$  not only the potential function in the intermediate phase 2, but also that in phase 1 is altered. For  $2d = 1/\kappa_2$  the partial potential in phase 1 is only 0.44 times that for  $2d = \infty$ ; for  $2d = \frac{1}{2\kappa_2}$  it is only 0.25 times that for  $2d = \infty$ . In the

equilibrium state we have therefore only an incomplete development of the electrical double layer. For  $2d = 1/2\kappa_2$ , for instance, also the double layer charge is only  $\frac{1}{4}$  of that for large dimensions of phase 2. For large values of  $D$  this mutual hindering of the double layers effects a less pronounced decrease of the particle charge, but in principle the same behaviour is found (cf. Appendix).

### 3. Conclusions Concerning the Stability of Emulsions.

On the basis of these considerations, we can now understand the fundamental difference between the primary stability conditions of emulsions and suspensoid sols:

(a) For oil-in-water emulsions (or generally emulsions where the drops have a lower dielectric constant) the smallest part of the double layer potential occurs in the outer, aqueous phase. Even for very large values of  $D$  (say 0.5 v.) we must expect that the potential drop in the outer, diffuse, layer is less than 100 mV. For very large values of  $D$ , it is true, the partition of  $D$  about the two phases tends to be less unequal (*cf.* the curves of Fig. 1 for  $D = 230$  mV. and  $D = 115$  mV.; see also Fig. 3 of our previous paper)<sup>1</sup>, but we have seen that large values of  $D$  are to be expected when the ionic concentration in one phase differs considerably from that in the second, and we read from Fig. 1 that in that case again the partial potential drop in the aqueous phase (phase with large  $\epsilon$ ) is very small.

Moreover, as soon as the oil drops are smaller than  $10^{-3}$  cm. ( $= 10\mu$ ), or  $10^{-4}$  cm. ( $= 1\mu$ ) in the most favourable case of a rather high  $\epsilon_2$  and a rather high electrolyte concentration in phase 2, the hindering effect described above occurs with the diffuse layer within the droplets and leads to another decrease of the  $\zeta$ -potential in the outer region of the double layer (*cf.* curves *a*, *b* and *c* of Fig. 2, where phase 2 corresponds schematically to the oil drops in the emulsion).

(b) For water-in-oil emulsions the potential drop in the outer diffuse layer will be higher, but here the critical  $\zeta$ -potential needed for primary stability is correspondingly higher. Moreover, the mutual hindering of the diffuse layers in the dispersion medium will play here an important role except for very dilute emulsions.

If one wishes to make use of equation (3) and not of the more experimental point of view based on the critical  $\zeta$ -potential and experimental data concerning the latter, one can summarise those factors (*a*) and (*b*) by stating that the double layer at the liquid-liquid interface, owing to the diffuse character of both layers, will have a smaller capacity than the double layer at the solid-liquid interface, and therefore, for equal double layer potentials, a smaller particle charge. The approximate equation (3) shows that the repulsion at contact is proportional to  $E^2$  ( $E$  = particle charge), and therefore considerably smaller in the case of an emulsion. A mutual hindering of the double layers, within the droplets, or between the particles, also leads to a decrease of the particle charge, and therefore equally to a weaker repulsion.

As a third factor decreasing the probability of a stable emulsion in comparison with suspensoids, we may refer briefly to the point already stressed in section 1: in the case of a solid wall very high values of  $D$  can sometimes be obtained by changing the concentration of the potential-determining electrolyte in the liquid medium; in the case of an emulsion it is not possible to vary the concentration in one phase only.<sup>17</sup>

### 4. The Function of Emulsifiers.

It is in accordance with these views that an emulsion can only be stabilised either with the aid of certain organic highly adsorbable ions,

<sup>17</sup> A mercury sol cannot be compared with the emulsions considered here; the mercury is a conductor and does not dissolve ions. The double layer potential is here of the order of + 800 to + 900 mV. (E. J. W. Verwey, *Diss.*, Utrecht, 1934, p. 70).

accumulating at the interface (such as soaps, salts of the higher fatty acids, the naphthenic acids, etc., and lyophobic colloids), or with the aid of all sorts of finely divided solids. Both have the effect of giving the liquid drops properties more or less comparable with that of solid particles, and of shifting again the double layer potential drop towards the outer phase.

With the first group of emulsifiers the double layer charge of the inner layer is present as a monomolecular layer of the active ions restoring the case that the charge can be considered as a true surface charge. The double layer potential drop occurs in the phase with the highest solving power of the counter ions.

As to the emulsifying action of finely divided solids, van der Minne has postulated that the emulsifying particles must be wetted better by the dispersion medium than by the disperse phase; the particles, trapped at the interface, will therefore cover the outside of the liquid droplets. Furthermore, the colloidal solid alone must give a stable sol in the dispersion medium. The largest part of the surface of the solid particles in the emulsion is in contact with this dispersion medium, and has a double layer of the same structure and electrical properties, as in this sol; if a sufficient part of the surface of the droplets is covered with these solid particles, the drops are surrounded by the same electrical field as the solid particles, their double layer has assumed the properties of a double layer of a solid substance, and the drops undergo the same repulsion as must be assumed for normal lyophobic colloids. In this respect it is noteworthy that the emulsifying action of these finely divided solids needs the presence of a small amount of electrolyte, and optimal emulsification occurs for electrolyte concentrations somewhat below the flocculation concentration of this electrolyte for the sol of the solid particles alone. This amount of electrolyte reduces the thickness of the outer layer of their double layer, and therefore reduces the mutual repulsion between these solid particles in the interface in such a way that they can be packed sufficiently densely on the surface of the droplets, and the properties of the liquid-liquid interface can be suppressed. Also the emulsifying action of finely dispersed solids can therefore easily be understood along these lines.

### Appendix.

We consider two large phases 1 separated by a layer of phase 2 (see Fig. 2). Since the problem is symmetrical we only have to consider the conditions on both sides of one interface; the zero point of the x-axis is therefore chosen in the left one. As in our previous paper<sup>1</sup> we measure the potential  $\psi_1$  in phase 1 from the level  $\phi_1$  for  $x = -\infty$ , the potential  $\psi_2$  in phase 2 from the level  $\phi_2$  for  $x = \infty$  in the case of an infinitely large distance of the interfaces. In phase 1 we have the unaltered solution of Gouy's differential equation:

$$\frac{d\psi_1}{d\xi_1} = e^{\frac{\psi_1}{2}} - e^{-\frac{\psi_1}{2}}$$

where  $y = \frac{e\psi(x)}{kT}$ ,  $\xi = \kappa x$ ,  $\kappa = \sqrt{\frac{8\pi e^2 n}{\epsilon kT}}$ . In phase 2 the solution is slightly

different owing to the different boundary condition halfway between the two interfaces:  $dy/d\xi$  is now zero at  $x = d$  instead of at infinity; calling

$u$  the  $y_2$  value at  $x = d$  ( $u$  being dependent on the distance  $2d$  of the interfaces), we have the solution :

$$\frac{dy_2}{d\xi_2} = -\sqrt{e^{y_2} + e^{-y_2} - e^u - e^{-u}} \quad (4)$$

Limiting ourselves to the interval  $0 < x < d$ , we must take in (4) everywhere the  $-$  sign. At the interface ( $x = 0$ ) we have the following conditions :

$$-y_1(0) + y_2(0) = -z_1 + z_2 = \Delta, \quad \left(\Delta = \frac{eD}{kT}\right)$$

and  $\epsilon_1 \left(\frac{dy_1}{dx}\right)_0 = \epsilon_2 \left(\frac{dy_2}{dx}\right)_0$  or  $\left(\frac{dy_1}{d\xi_1}\right)_0 = \alpha \cdot \left(\frac{dy_2}{d\xi_2}\right)_0$ ,

where  $\alpha = \frac{\kappa_2 \epsilon_2}{\kappa_1 \epsilon_1} = \sqrt{\frac{n_2 \epsilon_2}{n_1 \epsilon_1}}$

and therefore we find, using eq. (4), finally the following relation between  $z_2$  and  $u$  :

$$e^{d-z_2} + e^{z_2-d} - 2 = \alpha^2(e^{y_2} + e^{-y_2} - e^u - e^{-u}) \quad (5)$$

which for infinitely large distances of the interface (*i.e.*, for  $y_0 = 0$ ) reduces to the equations obtained in our previous paper I concerning the partition of the double layer potential about both phases :

$$z_2 = \ln \frac{\alpha + e^{\frac{d}{2}}}{\alpha + e^{-\frac{d}{2}}} \quad (5a)$$

In eq. (5) like in (5a)  $\Delta$  and  $\alpha$  are determined by the system. Eq. (5) contains both the unknown potentials  $z_2$  at the interface and  $u$  halfway between the interfaces, and we need, therefore, a second relation giving  $z_2$  and (or)  $u$  as a function of the distance  $d$ . This can be obtained by integrating eq. (4). The general solution of eq. (4) is an elliptic function. This elliptic function degenerates to an elementary function in two cases, *viz.*, small values of  $u$  and  $z_2$ , and large values of these quantities :

(a)  $u$  and  $z_2 \ll 1$  and everywhere  $y_2 \ll 1$ . The differential equation reads :

$$\frac{dy_2}{d\xi_2} = -\sqrt{y_2^2 - u^2}$$

with the solution (considering the boundary condition  $\xi_2 = \kappa_2 d$  for  $y_2 = u$ ) :

$$\kappa_2 d - \xi_2 = \ln \left( \frac{y_2 + \sqrt{y_2^2 - u^2}}{u} \right) \quad (6)$$

For  $\xi_2 = 0$  we find the desired relation between  $u$ ,  $z_2$  and  $\alpha$  which enables, together with eq. (5), the calculation of these quantities for given values of  $d$  :

$$\kappa_2 d = \ln \left( \frac{z_2 + \sqrt{z_2^2 - u^2}}{u} \right) \quad (6a)$$

If also  $\Delta$  is assumed to be small, eq. (5) reduces to :

$$\Delta - z_2 = \alpha \sqrt{z_2^2 - u^2} \quad (7)$$

and gives together with eq. (6a) the following relations for  $z_2 = f(d)$  :

$$z_2 = \frac{1 + e^{2\kappa_2 d}}{1 - \alpha + (1 + \alpha)e^{2\kappa_2 d}} \cdot \Delta \quad (8)$$

This equation has been used in calculating the data needed for the construction of Fig. 2; the corresponding values of  $u$  and  $y_2$  were calculated with the aid of eq. (7) and (6). Mostly the calculation can be simplified considerably for two reasons: (a) the interaction is especially important for values of  $d$  corresponding to  $\kappa_2 d \ll 1$ , and (b) the most important case for our considerations is that where phase 2, the intermediate phase, has the lowest dielectric constant, hence we can exclude the possibility  $\alpha > 1$ . If these conditions are fulfilled the eqs. (8) and (7) can be written:

$$\left. \begin{aligned} z_2 &= \frac{\Delta(1 - \alpha\kappa_2 d)}{\Delta} \\ \frac{u}{\Delta} &= \sqrt{\left(\frac{z_2}{\Delta}\right)^2 - (\kappa_2 d)^2} \end{aligned} \right\} \quad (9)$$

These equations appear to be already an excellent approximation in the case of curve (c) in Fig. 2 where  $\alpha = 0.1$  and  $\kappa d = 0.5$ . They show that the potential drop in phase 1 ( $\Delta - z_2$ ) and, therefore, also the double layer charge decrease proportionally with  $d$ .

(b)  $u$  and  $z_2 \gg 1$ . These conditions are generally fulfilled if  $z_2$  is not too small (say  $z_2 > 4$  or  $(\phi_2)_0 > 100$  mV.) and  $\kappa d$  is of the order 1 or smaller, and, therefore, in many problems concerning the interaction of two particles. Neglecting  $e^{-v_2}$  and  $e^{-u}$  in eq. (4) and solving the equation thus obtained we find:<sup>18</sup>

$$\xi_2 + C = 2e^{-\frac{u}{2}} \arcsin \left( e^{-\frac{y_2 - u}{2}} \right) \quad (10)$$

where  $C$  can be eliminated by considering the boundary condition  $y_2 = u$  for  $\xi_2 = \kappa d$ :

$$e^{-\frac{y_2 - u}{2}} = \cos \left( \frac{\kappa d - \xi_2}{2} \cdot e^{\frac{u}{2}} \right) \quad (10a)$$

$$\text{or} \quad e^{-\frac{z_2 - u}{2}} = \cos \left( \frac{\kappa d}{2} \cdot e^{\frac{u}{2}} \right) \quad (10b)$$

for  $\xi_2 = 0$  where  $y_2 = z_2$ . Eqs. (5) and (10b) give us together  $u$  and  $z_2$  as a  $f(d)$ . The double layer charge per  $\text{cm}^2$ :

$$\begin{aligned} q_0 &= \int_0^d \rho_2(x) dx = -\frac{\epsilon_2}{4\pi} \int_0^d \frac{d^2 \psi_2}{dx^2} dx = +\frac{\epsilon_2}{4\pi} \cdot \left( \frac{d\psi_2}{dx} \right)_0 \\ &= +\sqrt{\frac{\epsilon_2 kT \cdot n_2}{2\pi}} \cdot \left( \frac{dy_2}{d\xi} \right)_0 \end{aligned}$$

$$\text{or:} \quad q_0 = -\sqrt{\frac{\epsilon_2 kT \cdot n_2}{2\pi}} \cdot (e^{z_2} - e^u) \quad (11)$$

can then be calculated from  $z_2$  and  $u$ .

A numerical example will show that the eq. (5), (10b) and (11) lead to results similar to those calculated for small values of  $\Delta$  and given in Fig. 2.

**Example:**  $e^d = 10^4$  ( $\Delta = 9.2$ ;  $D = 230$  mV.) and  $e^{z_2} = 5 \times 10^3$  for  $2d = \infty$ ; then  $z_2 = 8.51$ ,  $\Delta - z_2 = 0.69$ . With the aid of eq. (5) we see that  $\alpha = 0.010$  in this case. In order to decrease  $\Delta - z_2$  from 0.69 to 0.46 ( $z_2 = 8.74$ ) we need (eq. (5)) a value of  $u = 8.32$ , and therefore (eq. (10b)) a distance of the interfaces  $\kappa_2 d = 0.02$ . If  $\kappa_2 = 10^3$  the distance  $2d$  amounts to  $0.4 \times 10^{-4}$  cm. As a consequence of this interaction we find (eq. (11)) a decrease of the double layer charge to 0.67 its original value. For a decrease of  $\Delta - z_2$  to 0.23 we find  $u = 8.88$ , and  $\kappa_2 d = 0.006$  or in our case  $2d = 0.12 \times 10^{-4}$ ; the corresponding decrease of the double layer charge is to 0.33 its original value.

<sup>18</sup> Similar equations for the case that phase 1 is a solid (and therefore  $z^*$  independent of  $d$ ) have been deduced recently by I. Langmuir, *J. Chem. physics*, 1938, 6, 873.

### Summary.

In the present paper we consider the question why a stable emulsion can never be obtained without the presence of a special emulsifier. From experimental data concerning aqueous lyophobic sols with solid particles it can be derived that the critical  $\zeta$ -potential for primary stability will be of the order of  $\pm 100$  mV.; in other media this  $\zeta$ -potential will be still higher. Assuming that the double layer originates from the ionic distribution equilibrium of electrolytes in the two liquid systems, it is shown that a sufficiently high  $\zeta$ -value can never be reached for the following reasons: (1) the concentration of a potential-determining electrolyte cannot be altered in one phase only, and the double layer potential is accordingly rather low; (2) the double layer has two diffuse layers, and the potential drop is divided up into two parts on both sides of the interface; (3) the development of the electrical double layer is restricted by the dimensions of the liquid phases (size of the drops, and their mutual distances in more concentrated emulsions), all factors leading to small values of  $\zeta$  and of the particle charge. Emulsifiers have the action of restoring some of the conditions existing in the case of a double layer at the interface of a solid and a liquid.

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## ON THE REPULSIVE FORCES BETWEEN CHARGED COLLOID PARTICLES AND ON THE THEORY OF SLOW COAGULATION AND STABILITY OF LYOPHOBE SOLS.

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It is most natural to ascribe the stability of sols, suspensions, and emulsions to forces of repulsion which arise when the particles approach each other and when the layer of the dispersion medium separating them becomes sufficiently thin.

At the same time, similar forces should play a decisive rôle in thixotropy and a number of other basic properties of colloidal and disperse systems. Such repulsive forces may be considered as being of two kinds:

1. Forces which are connected with the electrostatic interaction of ions in the ionic atmospheres of approaching micelles and
2. Forces of a different origin which are also observed in absence of electrolytes.\*

\* Since the appearance of the papers by Kruyt<sup>1</sup> and Bungenberg de Jong,<sup>2</sup> it is customary to consider solvation or hydration as the second stability factor of colloidal systems. However, up to the present the concept of solvation, applied to the stability of colloids, was qualitative in character only, which reflected the insufficiently precise and often contradictory meaning assigned to it by different authors. Thus, usually no clear distinction was made between the changes in the mechanical properties of solvated layers, and the changes in the thermodynamical properties which lead to the forces of interaction when particles approach. Hence, we shall avoid the use of the term solvation and speak instead of forces of the second kind, which are connected with the second thermodynamical

The forces of the first kind, in contrast with those of the second kind, can be treated theoretically on the basis of the theory of strong electrolytes as is shown in Part I. Part II will be concerned with the experimental method developed by the author in collaboration with M. Kussakov<sup>3</sup> to study the repulsive forces in thin layers. This method may be used to verify the theoretical calculations given in Part I and to study the forces of the second kind.

In what follows, an important rôle is played by the following formula which by means of calculations, permits passing from the short range interaction (of any nature) between plane surfaces to the interaction between spherical surfaces (see Fig. 1):

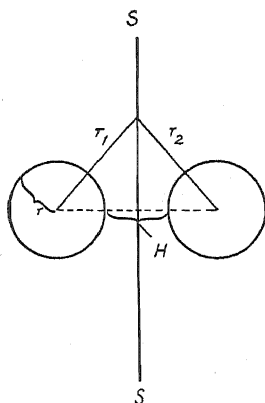


FIG. 1.

$$N = \pi r \int_H^{\infty} P(h) dh, \quad (1)$$

where  $P(h)$  is the force of repulsion (or attraction) per unit area between plane parallel surfaces separated by a liquid layer of thickness  $h$ , and  $N$  is the force of repulsion between spherical surfaces of the same nature, whose radius is  $r$ , submerged in the same liquid and separated at the distance of closest approach by  $H$ .

As follows from its derivation,<sup>4</sup> formula (1) holds for large values of the ratio  $r/d$ , where  $d$  is the effective radius of action of the repulsive forces between the surfaces.

## Part I. The Theory of Repulsive Forces of Electrostatic Origin.

### 1. Calculation of the Interaction of Spherical, Charged Particles.

It is necessary in the first place to consider the Debye-Hückel equation for small values of the potential  $\psi$  having the following form:

$$\Delta\psi = k^2\psi \quad (2)$$

where  $k = 1/d$ , the reciprocal of the Debye thickness  $d$  of ionic atmospheres, may be computed by means of the formula:

$$k = \sqrt{\frac{8\pi F}{DRT} \sum \frac{z_i^2 \gamma_i}{2}} \quad (2')$$

where  $F$  is the Faraday number,  $D$  is the dielectric constant of the medium,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\gamma_i$  is the

criterion of solvation which has just been mentioned. It should be pointed out that the lack of lucidity and the discordance, which are connected with the usage of the concept of solvation are mainly due to the fact that, until only recently, no theoretical or direct experimental approach to a study of the properties of thin, polymolecular liquid layers existed.

<sup>1</sup> Krut, *Z. physik. Chem.*, 1922, 100, 250.

<sup>2</sup> Bungenberg de Jong, *Het Agarsol, Dissert.*, Utrecht, 1921.

<sup>3</sup> B. Derjaguin and M. Kussakov, *Bull. Acad. Sci. U.R.S.S., Sér. Chim.*, 1937, 5, 1119 (in russ.); *Acta Physicochimica U.R.S.S.*, 1939, 10, 25; 1939, 10, 153.

<sup>4</sup> B. Derjaguin, *Koll. Z.*, 1934, 69, 155.

molality of the  $i$ th ion and  $z_i$  is its valence (the number of elementary charges).

Assuming that the electrolyte is of the type I—I, the approximate equation (2) may be employed when the following condition is fulfilled:

$$\psi < 50 \text{ mV.} \quad (2'')$$

Furthermore, we will assume that the following condition holds at the surfaces of particles:

$$\psi = \psi_0 = \text{const.}, \quad (3)$$

where  $\psi_0$  is independent of the mutual location of the surfaces.

Having determined  $\psi$  by means of (2) and (3) one may find the forces applied to the surfaces, by adding to the expressions for Maxwell's stresses the term expressing the excess osmotic pressure  $\Delta p$ , which is equal to

$$\Delta p = \frac{D}{8\pi} k^2 \psi^2. \quad (4)$$

A determination of the interaction of flat surfaces\* according to this method yields the following expression for  $P(h)$ :

$$P(h) = \frac{D}{8\pi} \frac{k^2 \psi_0^2}{\cosh(kh/2)}. \quad (5)$$

Hence, with the aid of equation (1), the following expression is obtained:<sup>5</sup>

$$N = \frac{D}{4} r \psi_0^2 \left[ 1 - \text{tgh.} \left( \frac{kH}{2} \right) \right], \quad (6)$$

where

$$\tau = kr = \frac{r}{d}. \quad (7)$$

The approximation (6) is applicable when

$$\tau = \frac{r}{d} \gg 1. \quad (7')$$

For the energy of interaction at constant potentials,  $U_\psi(h)$ , one obtains<sup>5</sup> from equation (6):

$$U_\psi(H) = \int_H^\infty N_\psi dH = \frac{D}{2} r \psi_0^2 \ln(1 + e^{-kH}). \quad (8)$$

In order to calculate the interaction of micelles whose dimensions are comparable to  $d$ , one may use the formula:

$$N = \frac{D}{8\pi} \iint [|\text{grad } \psi|^2 + k^2 \psi^2] dS, \quad (9)$$

\* The first computations of this kind were carried out by the author in 1935<sup>5</sup> for plane surfaces and for spherical surfaces having a slight curvature. For the case of plane surfaces, similar computations, on the basis of the exact Debye-Hückel equation, were carried out by P. Bergmann, P. Löw-Beer, and H. Zocher<sup>6</sup> (1938), A. Frumkin<sup>7</sup> (1938) and I. Langmuir<sup>8</sup> (1938). However, P. Bergmann, P. Löw-Beer, and H. Zocher, instead of condition (3), introduced the condition that the charges of the plates are constant, which is less natural.

<sup>5</sup> B. Derjaguin, *Bull. Acad. Sci. de l'U.R.S.S., Sér. chim.*, 1937, 5, 1153; *Acta Physicochimica U.R.S.S.*, 1939, 10, 333.

<sup>6</sup> P. Bergmann, P. Löw-Beer, and H. Zocher, *Z. physik. Chem., A*, 1938, 181, 301.

<sup>7</sup> A. Frumkin and A. Gorodetzkaia, *Acta Physicochimica U.R.S.S.*, 1938, 9, 327.

<sup>8</sup> I. Langmuir, *Science*, 1938, 88, 430, Nov. 4; *J. Chem. Physics*, 1938, 6, 873.



in which the integral is taken over the whole plane of symmetry  $S$  (see Fig. 1).

In (9) the first term under the integral sign corresponds to the electrical vector which, from considerations of symmetry, lies in the plane  $S$  and therefore gives rise to a pressure in a direction normal to this plane. The final value of  $N$  and, consequently,  $U_\psi$ , depends upon what approximate value of  $\psi$  we will substitute into this formula. If we take for  $\psi$  the superposition of the potentials produced by each micelle in the absence of another, we obtain :

$$U_\psi = U_Q = D\psi_0^2 r^2 \frac{e^{-kH}}{(2r+H)} = \frac{Q^2}{D} \frac{e^{-kH}}{(\tau+1)^2(2r+H)}, \quad (10)$$

where  $Q$  is the total charge of each of the micelles.

This expression is more exact, at least for large values of  $kr = \tau$ , than the formula proposed by H. Hamaker :<sup>9</sup>

$$U = \frac{Q^2}{D} \frac{e^{-kH} \cdot e^{-\tau}}{(\tau+1)(2r+H)} = D\psi_0^2 r^2 \frac{(\tau+1)e^{-(kH+\tau)}}{(2r+H)} \quad (10')$$

since in the limiting case, for  $H = 0$  and very large values of  $\tau$ , when formula (8) is exactly applicable, formula (10) differs from (8) in the ratio  $1 : \ln 2$ , while formula (10') differs from (8) in the ratio

$$(1+\tau)e^{-\tau} : \ln 2,$$

i.e., (10') gives a result which is incorrect even with respect to its order of magnitude.

In order to obtain a more precise value for  $N$ , one may make use of the approximate value for  $\psi$  obtained by S. Levine,<sup>10</sup> this value being the more exact the larger the value of  $kH$  :

$$\psi = \frac{Q_0 e^\tau}{D(1+\tau)} \frac{1}{1-\delta_1} \left( \frac{e^{-kr_1}}{r_1} + \frac{e^{-kr_2}}{r_2} \right), \quad (11)$$

where  $r_1$  and  $r_2$  are the distances to the centres of the first and second micelles, respectively, and

$$\delta_1 = \frac{e^\tau (\tau \cosh \tau - \sinh \tau)}{1+\tau} \frac{e^{-k(2r+H)}}{k(2r+H)}. \quad (11')$$

Omitting the details of the calculations, we shall give the expressions for  $U_Q$ —the energy of interaction at constant charges, and  $U_\psi$ —at constant potentials, which can be obtained from (9) and (11) :

$$U_Q = \frac{Q_0^2}{D(\tau+1)^2(1-\delta_1)} \frac{e^{-kH}}{(2r+H)}, \quad (12)$$

$$U_\psi = D\psi_0^2 r^2 \frac{\frac{e^{-kH}}{2r+H}}{1 + \frac{e^{-\tau} \sinh \tau}{2\tau} \cdot \frac{2r e^{-kH}}{2r+H}} \quad (12')$$

If condition (7') is fulfilled it becomes possible to find such values for  $H$  that simultaneously

$$r \gg H \gg d;$$

<sup>9</sup> H. Hamaker, *Rec. Trav. chim. Pays-Bas*, 1937, 56, 3, see p. 25; also, *ibid.*, 1936, 55, 1015.

<sup>10</sup> S. Levine, *Proc. Roy. Soc.*, 1939, 170, 145, 165.

for this range of values for  $H$  both formulæ, (8) and (12'), being sufficiently precise, yield the same values for  $U_\psi$ :

$$U_\psi \simeq \frac{Dr\psi_0^2}{2} e^{-kH},$$

i.e., they have a region of coincidence. We can combine both these formulæ into one as follows:

$$U_\psi = \frac{Dr\psi_0^2}{2} \ln \left\{ 1 + \frac{\frac{2r}{2r+H} e^{-kH}}{\left[ 1 + \frac{e^{-\tau} \sinh \tau}{2\tau} \frac{2r e^{-kH}}{(2r+H)} \right]} \right\}, \quad (13)$$

which, when  $kH$  is small, reduce to (8), and when  $kH$  is large, to (12'). This expression may be employed to interpolate the values of  $U_\psi$  in the range of average values of  $kH$ . Such an interpolation, which is the more exact the greater the ratio  $\frac{r}{d} = kr = \tau$ , may give a certain error when this ratio is small; but the magnitude of this error when these computations are applied to the theory of colloids cannot have any significance.

It should be noted that even for the most disadvantageous case for formula (13), when  $\tau = 0$ , which corresponds to the interaction of charged spheres in the absence of ionic atmospheres, formula (13) gives results which are quantitatively not much different from those obtained when the corresponding electrostatic problem is solved exactly.

In particular, when  $\tau = 0$  and  $H = 0$ , formula (13) gives:

$$U_\psi(0) = \frac{Dr\psi_0^2}{2} \ln \frac{5}{3} = 0.256 \dots Dr\psi_0^2, \quad (14)$$

while the exact value is <sup>11</sup>:

$$U_\psi(0) = (1 - \ln 2) Dr\psi_0^2 = 0.307 \dots Dr\psi_0^2. \quad (14^I)$$

The second approximation, obtained by S. Levine,<sup>10</sup> if it were used instead of the first approximation, would give a still more exact result. This follows from the fact that, at  $\tau = 0$ , for  $U_Q(0)$  S. Levine gets:

$$U_Q(0) = \frac{23}{52} \frac{Q_0^2}{Dr} = 0.442 \dots \frac{Q_0^2}{Dr} \quad (14^{II})$$

which differs very slightly from the exact value: \*

$$U_Q(0) = \left( \frac{1}{\ln 2} - 1 \right) \frac{Q_0^2}{Dr} = 0.443 \dots \frac{Q_0^2}{Dr}. \quad (14^{III})$$

Thus we may regard (13) as a universal formula, which is approximately applicable for any values of  $d$ ,  $r$ , and  $H$ . In Fig. 2 there are given curves for  $U_\psi(H)$  as a function of  $H$  for several values of  $\tau$ , calculated with the aid of (13).

When  $H = 0$ , we obtain from (13):

$$U_\psi(0) = \frac{Dr\psi_0^2}{2} \ln \left( 1 + \frac{1}{1 + \frac{e^{-\tau} \sinh \tau}{2\tau}} \right), \quad (14^{IV})$$

<sup>11</sup> J. Jeans, *The Mathematical Theory of Electricity and Magnetism*, p. 290, example 36 (5th ed.) Cambridge, 1927.

\* S. Levine, employing an erroneous value for  $U_Q(0)$  instead of (14<sup>III</sup>), did not find such a good agreement with his formula, and for this case (for  $\tau = 0$ ) he underestimated its accuracy.

from which we see that  $U_\psi(o)$  depends only slightly upon the thickness  $d$  of the ionic atmospheres, only changing in the ratio  $\ln 2 : \ln 5/3$  with a change in  $d$  from 0 to  $\infty$ .

## 2. The Free Energy of Charged Particles.

A paper by S. Levine<sup>10</sup> also contains a calculation of  $U_Q$ . Comparing our formula, (12), with his formula, (35''), we find that our

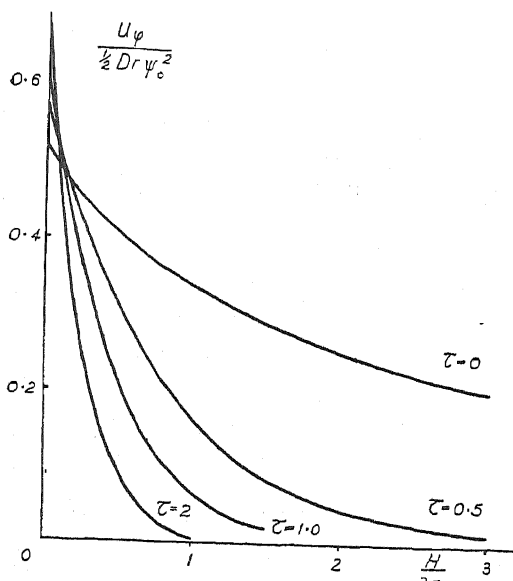


FIG. 2.

formula differs from Levine's by the absence of the second, negative term in its right-hand side. It is easy to show that this negative term appeared on account of the incorrect expression for the free energy of charged particles in the electrolyte.

The error made is very essential, leading, for example, to the conclusion that, at sufficiently large distances, particles (and also parallel plates) having the same charge sign are attracted, though this is directly refuted by our formula (9).

On account of this, it is of interest to derive a correct general expression for the free energy of charged surfaces in an electrolyte.

With this aim in view, let us consider a system consisting of  $p$  conductors of finite dimensions and a  $(p+1)$ th conductor possessing a very large surface and, therefore, a large capacity ("earth"), submerged in an electrolyte whose volume is  $v$ . Denoting the Gibbs-Helmholtz free energy by  $F$ , the charge and the potential of the  $i$ th conductor by  $Q_i$  and  $\psi_i$ , respectively, its co-ordinates by  $x_i$ ,  $y_i$ ,  $z_i$ , and the corresponding components of the forces acting on the  $i$ th conductor by  $X_i$ ,  $Y_i$ ,  $Z_i$ , for the case when the volume  $V$  remains constant we may write:

$$dF = \sum_{i=1}^{i=p} \psi_i dQ_i - \sum_{i=1}^{i=p+1} (X_i dx_i + Y_i dy_i + Z_i dz_i). \quad (15)$$

The term expressing the work of charging the  $(p+1)$ th conductor is absent since its potential does not differ appreciably from zero; moreover, the system as a whole remains electrically neutral if the condition

$$Q_{p+1} + \sum_{i=1}^{i=p} Q_i = 0 \quad . \quad . \quad . \quad (15')$$

is fulfilled.

No other terms should be introduced into the right-hand side since the macroscopical state of the system is completely defined by the parameters  $V, Q_i \dots, x_i \dots, y_i \dots, z_i \dots$ , for example, the introduction into (15) of a member expressing the work of charging the ionic atmospheres, as is done by S. Levine, is not correct because the densities of the charges in the ionic atmospheres correspond to the "uncontrolled" co-ordinates and are established on account of the thermal motion.

The source of S. Levine's error consists in an incorrect usage of Debye's method of charging ions (and micelles in the case of Levine) which, as is known, permits one to find the free energy of an electrolyte. When Debye's method is used, it is necessary that the charges of *all* the ions, independent of their *co-ordinates*, increase proportionally to the same parameter  $\lambda$ . However, S. Levine does not observe this necessary condition in employing Debye's method, and this follows particularly clearly from his discussion<sup>10</sup> on page 179, in which S. Levine, while bringing to completion the charging of the ions with a sign opposite to that of the micelle, transfers charges only to that (in reality small) part of the ions which is present in the region of the ions atmosphere, thus letting the rest of the ions become charged only when they get into this region as a result of thermal motion. It may be shown<sup>12</sup> that a rigorous and consistent use of Debye's method leads to results which coincide with those which we obtained thermodynamically.

Integrating (15) keeping  $x_i, y_i, z_i \dots$  as constants, we get:

$$F = \sum \int_0^{Q_i} \psi_i dQ_i; \quad (16)$$

the omitted constant of integration is independent of the charges and co-ordinates  $x_i, y_i, z_i$ , for the discharged conductors do not interact (if we disregard the effects depending upon the electrical images of the ionic atmospheres in the surfaces of the conductors and leading to repulsion of the approaching surfaces).

Within the limits of applicability of equation (2), the capacity of the conductors in the electrolyte remains constant while they are being charged and therefore instead of (16) we may also write:

$$F = \frac{1}{2} \sum \psi_i Q_i. \quad (16')$$

According to (15), the work of separation (the sign reversed) of conductors of constant charges to an infinite distance, equal to  $U_0$ , is:

$$U_0 = F - F_\infty = \sum \int_0^{Q_i} \psi_i dQ_i - \sum \int_0^{Q_i} (\psi_i)_\infty dQ_i \quad (17)$$

where the subscript  $\infty$  refers to the final configuration; or, when the capacity remains constant:

$$U_0 = \frac{1}{2} \sum \psi_i Q_i - \frac{1}{2} \sum (\psi_i)_\infty Q_i = \frac{1}{2} \sum [\psi_i - (\psi_i)_\infty] Q_i \quad (17')$$

Applying (15) to the similar process of removing conductors at constant potentials, and then taking into account (16), and the constancy of capacity we get:

$$U_\varphi = F - F_\infty - \sum \psi_i [Q_i - (Q_i)_\infty] = - \sum \int (Q_i) d\psi_i + \sum \int (Q_i)_\infty d\psi_i \quad (17'')$$

$$U_\varphi = - \frac{1}{2} \sum \psi_i Q_i + \frac{1}{2} \sum \psi_i (Q_i)_\infty = - \frac{1}{2} \sum \psi_i [Q_i - (Q_i)_\infty] \quad (17''')$$

<sup>12</sup> A more detailed account of these and related calculations is in the process of publication in *Acta Physicochimica U.R.S.S.*

Transforming the expression (16') with the aid of Green's theorem and Poisson's equation, it assumes the following form :

$$F = \frac{D}{8\pi} \iiint \{ |\text{grad } \psi|^2 \} dv + \frac{Dk^2}{8\pi} \iiint \psi^2 dv \quad (18)$$

The first term in the right-hand side of this equation represents the usual expression for the free energy of an electrical field; the second term represents the change in the osmotic free energy of the ions, which occurred as a result of a redistribution of the ions after the charging of the micelles.

It is easy to verify<sup>12</sup> that our  $F$  satisfies the Gibbs-Helmholtz equation :

$$F - T \frac{\partial F}{\partial T} = \left( D + T \frac{\partial D}{\partial T} \right) \frac{1}{8\pi} \iiint |\text{grad } \psi|^2 dV = W \quad (19)$$

where  $W$  is the internal energy of the electrical field.

Using equations (17') and (17''), it is also easy to obtain the approximate equations of interaction of micelles (12) and (12'), and, moreover, using (18) to prove the equivalence of the obtained expressions for the energy to Maxwell's stresses to which excess osmotic pressure is added.\*<sup>12</sup>

### 3. The Theory of Slow Coagulation and Stability of Lyophobic Colloids.†

As already shown,<sup>13</sup> the velocity of the slow coagulation of sols,  $v$ , which is equal to the number of aggregation acts in 1 cm.<sup>3</sup> per second, is given by the equation :

$$v = \frac{4\pi\delta c^2}{\int_0^\infty \frac{e^{\frac{UH}{KT}}}{(2r+H)^2} dH} \quad (20)$$

where  $U(H)$  is the energy of interaction of the particles;  $\delta$  is the diffusion coefficient of the particles; and  $c$  is the particle concentration. Understanding by the stability  $L$ , a quantity<sup>14</sup> inverse to  $v$ , for the increase in stability in comparison with the minimum stability  $L_0$  corresponding to  $U = 0$  (rapid coagulation) we obtain the expression :

$$\frac{L}{L_0} = \int_0^\infty \frac{e^{\frac{UH}{KT}}}{(2r+H)^2} 2r dH \quad (21)$$

Substituting into this expression the value for  $U_\psi$  given by (13),‡ we get :

\* The author wishes to express his thanks to Professors A. N. Frumkin, L. I. Mandelstam, J. E. Tamm, and M. A. Leontovich for their friendly discussion of these results.

† The fundamental results in this field were obtained considerably earlier (1935).<sup>5</sup>

‡ This is equivalent to ignoring the forces of another, not electrostatic, origin and ascribing to the cohesion forces, which bring about the aggregation of the particles, an infinitely small radius of action. For a detailed discussion of the  $U$  vs.  $H$  diagram in general case which include Van der Waals attractive forces see by H. Freundlich,<sup>15</sup> H. Hamaker,<sup>16</sup> and R. Houwink and W. Burgers.<sup>17</sup>

<sup>13</sup> N. Fuchs, *Z. Physik*, 1934, 89, 736.

<sup>14</sup> P. Reh binder and E. Wenström, *Koll. Z.*, 1930, 53, 145.

<sup>15</sup> H. Freundlich, *Thixotropy* (Paris, 1935).

<sup>16</sup> H. Hamaker, *Rec. Trav. Chim. Pays-Bas*, 1936, 55, 1015; 1937, 56, 1; 1937, 56, 727; 1938, 57, 61; *Physica*, 1937, 4, 1058.

<sup>17</sup> R. Houwink and W. Burgers, *Elasticity, Plasticity and Structure of Matter*, see especially pp. 338-343. (Cambridge University Press, 1937.)

$$\frac{L}{L_0} = \int_0^\infty \left\{ 1 + \frac{\frac{2r}{(2r+H)e^{-kH}}}{1 + \frac{e^{-\tau} \sinh \tau}{2\tau} \frac{2r e^{-kH}}{(2r+H)}} \right\}^{\frac{Dr\psi_0^2}{2kT}} \frac{2r dH}{(2r+H)^2} \quad (22)$$

Letting  $kH$  equal  $2\tau\gamma$ , we get :

$$\frac{L}{L_0} = \int_0^\infty \left[ 1 + \frac{1}{(1+z)e^{2\tau\gamma} + \frac{e^{-\tau} \sinh \tau}{2\tau}} \right]^n \frac{dy}{(1+y)^2} \quad (22')$$

where 
$$n = \frac{Dr\psi_0^2}{2kT}; \quad . \quad . \quad . \quad (23)$$

for very large values of  $\tau$  it is more convenient to substitute  $z$  for  $kH$ , and then we get as a further approximation,

$$\mathcal{F}_n = \frac{L}{L_0} = 1 + \frac{1}{2\tau} \int_0^\infty [(1+e^{-z})^n - 1] dz. \quad (22'')$$

We observe that the stabilising action of ionic atmospheres,  $\frac{L}{L_0}$ , may be represented by a function of two dimensionless parameters,  $n$  and  $\tau$  :

$$\frac{L}{L_0} = \mathcal{F}(n, \tau) \quad . \quad . \quad . \quad (24)$$

An analysis of the integral appearing in (22''), shows that, for given  $n$ ,  $\mathcal{F}$  depends only slightly upon  $\tau$ ; on the contrary, for a given  $\tau$ ,  $\mathcal{F}$  increases rapidly with an increase in  $n$ , reaching very large values when  $n \cong 10$ . As an example, in Fig. 3 we give a graph of the function  $\mathcal{F}_n$  (the factor  $\frac{1}{2\tau}$  being taken as unity).

In (23), letting  $n = 10$ ,  $D = 80$ , and  $r = 10^{-6}$  cm.,  $T = 290$ , we find that sols of such a dispersity are sufficiently stable when

$$\psi_0 > 30 \text{ mV.},$$

which is in accord with the experimental data on the critical value of the  $\zeta$ -potential, which may be identified with  $\psi_0$ .

When the values of  $r$  are smaller, the critical values of the  $\zeta$ -potential may happen to be greater, however, in this case, the whole theory and, consequently, equation (23) may lose their applicability since condition (2'') is not fulfilled.

Limiting ourselves to the case when  $r > 0.4 \cdot 10^{-6}$  cm., we may state that for given  $r$  the limit of stability is determined mainly by the  $\zeta$ -potential, and depends only slightly upon  $\tau$ , and consequently upon  $d$ . This conclusion, however, is correct only when  $d$  is substantially greater than the effective radius of action of the attractive forces.

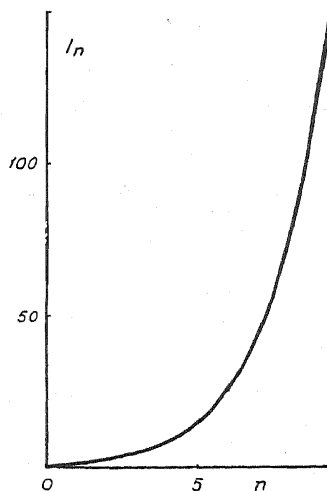


FIG. 3.

## Part II. The Experimental Approach to a Study of the Forces of Repulsion between Surfaces Separated by Liquid Films.\*

In order to obtain a direct experimental check of the above calculations of the pressure exerted by a layer of an electrolyte, or in general by a layer of some liquid, it is convenient to make use of the method which was developed before.<sup>8</sup> This method serves to determine the dependence of the pressure,  $P$  (which we termed disjoining pressure), developed by a thin wetting film, upon its thickness  $h$  (disjoining pressure isotherms).

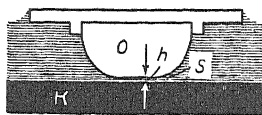


FIG. 4.

This method consists in a simultaneous measurement (see Fig. 4) of the *equilibrium* thickness  $h$  of the wetting film,  $S$ , which is formed between a bubble  $O$  and a plane surface of a body  $K$ , to which this bubble is pressed, and the capillary pressure  $P$  existing within the bubble and calculated according to the Laplace law. While measurements are being made, the capillary pressure,  $\bar{P}$ , is, as it were, balanced by the disjoining pressure,  $P$ , developed by the film at a given thickness of the latter.

In order to measure  $h$ , we made use of a microscopic observation (see Fig. 4) of the interference pattern obtained when the film  $S$  was illuminated by means of a vertical illuminator; thus it was possible to obtain single valued determinations of the thickness, accurate to 5-10 m $\mu$ , made possible due to a special method connected with the use of a monochromator as a light source, which permitted the wave-length of the light to be varied continuously.

In Fig. 5, we give the obtained isotherms of the disjoining pressure for different concentrations of NaCl solutions on a lead glass. In order to check the applicability of the theory of strong electrolytes, we cannot use formula (5) directly, since it refers to the case of a film bounded on both sides by the same surfaces. Moreover, it is based on the assumption that condition (2'') is fulfilled, which could not be guaranteed in our experiments. However, we can make use of the calculations of A. Frumkin and A. Gorodetskaja,<sup>7</sup> which relate precisely to the case of wetting films considered here; these authors showed that, if one boundary surface of the film is charged to the potential  $\psi_0 \gg \frac{2RT}{F}$ , while the

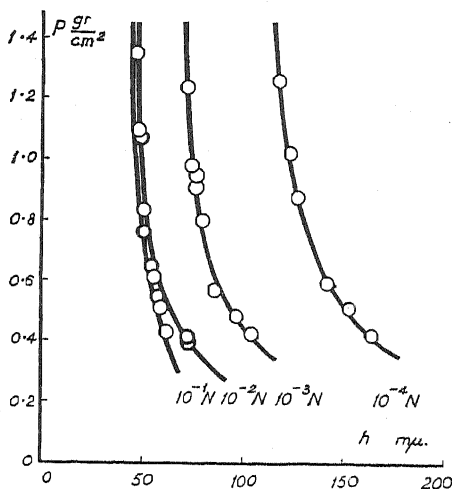


FIG. 5.

other surface separating it from the air carries a free charge equal to zero and  $h \gg d$ , then, as an approximation,

$$P = \frac{8 \left( \frac{kT}{D} \right)^2}{\pi d^2} e^{-\frac{2h}{d}} \quad (25)$$

\* By B. Derjaguin, M. Kussakov and A. Titijevskaja.

In Table I a comparison is given of the values of  $P$ , found for  $h = 115 \text{ m}\mu$  and for  $h = 75 \text{ m}\mu$ , with the values calculated according to formula (25) as a function of the concentration  $\gamma$ ;  $d$  in (25) was calculated by means of formula (2').

TABLE I.

$h = 115 \text{ m}\mu$ .			$h = 75 \text{ m}\mu$ .		
$\gamma$	$P_{\text{exp.}}$	$P_{\text{calc.}}$	$\gamma$	$P_{\text{exp.}}$	$P_{\text{calc.}}$
$10^{-4} \text{ N.}$	1500 dyn./cm.	2 dyn./cm.	—	—	—
$10^{-3} \text{ N.}$	400 „	$2 \times 10^{-6}$ „	$10^{-3} \text{ N.}$	1000 dyn./cm.	0.006 dyn./cm.

Hence it is seen that agreement is lacking<sup>18</sup> even with respect to the order of magnitude of the pressure. (Compare <sup>6</sup>.)

We have a similar picture for the case of an aqueous solution of  $\text{BaCl}_2$  also.

We see that the theory of strong electrolytes in this case ceases to hold at lower concentrations than it usually does and that apparently forces of another, non-electrostatic origin exist,<sup>3, 18</sup> responsible for the pressure of these films, especially for concentrated solutions of electrolytes on glass (and other *hydrophile* surfaces as, for example, mica,<sup>3</sup> diamond,<sup>18</sup> quartz).

The existence of such forces can be considered as definite particularly on the basis of the application of our method to a study of the wetting films of non-aqueous liquids<sup>3, 18</sup> not containing ions.

As an illustration, in Fig. 6, we give the data for *n*-heptane (circles) on steel and *n*-hexyl alcohol (cross) on glass. By points, we give data which show the increase of the effect upon the addition of 0.001 mol./l. of *n*-caprylic acid to heptane (on steel).

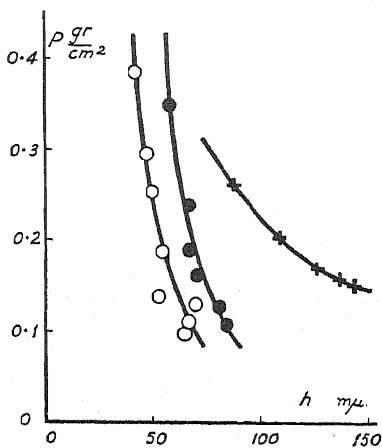


FIG. 6.

Similar effects of increase and sometimes decrease were found in the majority of the other systems studied. It may be shown thermodynamically that such an effect irrefutably points to the diffuseness of adsorption layers in solutions.<sup>18</sup> The existence of these  $\frac{\partial P}{\partial \gamma}$ -effects evidently may be

connected with the effect of dissolved substances (emulsifiers and stabilisers) upon the stability of colloidal and disperse systems.<sup>3, 19</sup>

The possibility of observing a measurable pressure  $P$  in the case of polymolecular films for almost all the liquids investigated demonstrates the universal significance of the forces of the second kind. Together with this, these experiments may be regarded as a proof of W. B. Hardy's views,<sup>20</sup> who foretold the existence of this pressure, and as a proof of the relatively large radius of molecular action of surfaces upon neighbouring liquid layers. The pressure  $P$  which we observed, however, cannot be ascribed to the van

<sup>18</sup> See also B. Derjaguin, M. Kussakov and L. Lebedeva, *C.R. Acad. Sci. U.R.S.S.*, 1939, 23, No. 7.

<sup>19</sup> B. Derjaguin, *Mineral Resources*, 1934, 9, 33 (in Russ.).



der Waals' forces, *e.g.*, dispersion forces, which are additive in the sense of F. London. As a proof of this,<sup>18</sup> one may cite the disappearance of *P* (rupture of the film) in the case of water if the surface of glass (or another hydrophile body) is previously coated with a monolayer of calcium stearate (according to the method of J. Langmuir and K. Blodgett<sup>21</sup>) or paraffin. This circumstance is essential because, if the forces of the second kind reduced to the dispersion forces, then, on account of the property of these latter forces, proved by H. Hamaker,<sup>22</sup> they could not lead to repulsion between similar micelles, *i.e.*, could not serve as a stability factor in colloids.

On the other hand, the presence of disjoining pressure in the case of heptane shows that it is independent of dipole forces also.<sup>3</sup>

Thus the nature of the effect is not clear, and a theoretical treatment is as yet impossible.

However, since this pressure should play a basic rôle in the aggregative stability of colloidal systems, the developed experimental method for measuring this pressure should be of particular importance.

In order to be able, with the aid of formula (1), to pass from results of such measurements on macro-surface to the forces acting between colloid or disperse particles, it is necessary, however, to measure the pressures *P* of the film confined between identical surfaces. Such measurements, preliminary in character, have already been carried out<sup>23</sup>; at present a new, more perfect procedure for such measurements is being developed in our laboratory.

### Summary.

1. A formula is given which permits to pass from the interaction of plane surfaces to the interaction of spherical ones separated by the same liquid.

2. On the basis of the theory of strong electrolytes, calculations are given of the force and energy of interaction between spherical conductors (micelles) immersed in an electrolyte. The derived equation may be applied with a sufficient degree of accuracy to any values of the radius, of the distance between micelles, and of the thickness of the ionic atmospheres.

3. General expression for the free energy of charged conductors in electrolytes is given.

4. Calculations of the energy of interaction of micelles are used to calculate the velocity of slow coagulation and stability of lyophobic sols and suspensions as functions of their  $\zeta$ -potential.

5. It is shown that, while the radius of action of attractive forces is small in comparison with the thickness of ionic atmospheres, stability of lyophobic systems fundamentally depends upon the parameter :

$$n = \frac{Dr\psi_0^2}{2kT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and depends only slightly upon the thickness of the ionic atmospheres. Sufficient stability is obtained when  $n = 10$  and the value for the critical  $\zeta$ -potential calculated from this, using  $r = 10^{-6}$  cm., is approximately 30 mV.

6. A method was pointed out for the measurement of the forces of repulsion (pressure) exerted by thin polymolecular liquid films.

The data obtained in this way show for glass and other hydrophile surfaces great deviations with theory based on the equation of Debye-Hückel at average and high concentrations, which points to the presence of a non-electrostatic mechanism of this effect.

<sup>20</sup> See *e.g.* W. B. Hardy, *Phil. Trans. (A)*, 1931, **230**, 1.

<sup>21</sup> See *e.g.* K. Blodgett, *J. Physic. Chem.*, 1937, **41**, 975.

<sup>22</sup> H. Hamaker, *Physica*, 1937, **4**, 1058.

<sup>23</sup> B. Derjaguin and E. Obuchov, *Acta Physicochimica U.R.S.S.*, 1936, **5**, 1.

7. For the majority of the liquids investigated, among which are organic liquids, the pressure of thin films decreases to zero only when its thickness is of the order of  $0.2-0.3 \mu$ , which points to the comparatively large radius of action of surfaces upon the neighbouring liquid layers.

8. Proofs are given that the forces responsible for these effects are neither of the nature of van der Waals' forces nor of the nature of dipole forces.

9. The pressure of thin layers of liquids to a great extent depends upon the concentration of dissolved molecules, among them non-electrolytes also, and this may be connected with the diffuseness of adsorption layers in non-electrolytic solutions as well. This effect may be used to explain the mechanism of the stabilising action of surface-active substances.

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## STABILITY PROPERTIES IN HYDROPHOBIC SOLS; APPLICATION OF THE MUTUAL ENERGY OF TWO PARTICLES.

BY S. LEVINE AND G. P. DUBE.

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### 1. Introduction.

In this paper we shall give a number of applications of the expression for the mutual energy of two colloidal hydrophobic spherical particles, developed by us in earlier papers.<sup>1</sup> We shall deal only with the first approximation to the electrical energy, corresponding to linear superposition of the diffuse layers and fairly satisfactory for  $\kappa a < 10$  (about) where  $\kappa$  is the characteristic quantity in the Debye-Hückel theory and  $a$  is the radius of a particle. For larger  $\kappa a$ , there may be a considerable correction for the distortion effect. However, we may expect that the first approximation will illustrate quite well many of the important properties associated with stability of the sol.

On adding the electrical and van der Waals energy for two particles, the resultant energy function exhibits a maximum close to contact and a minimum at larger separations. Here we shall discuss the behaviour of the maximum and also of the energy at contact. Adopting the method suggested by Hamaker,<sup>2</sup> we illustrate graphically the properties of the energy function by drawing constant energy contours in two-dimensional planes whose axes are suitable pairs of the chief quantities that may be varied experimentally, namely particle charge  $Q$ , radius  $a$ , electrokinetic potential  $\zeta$  and electrolyte concentration  $\gamma$  (mol./l.). Such diagrams prove to be very useful in determining stability properties of a sol. The application of our results to slow coagulation is also briefly indicated.

<sup>1</sup> Levine, *Proc. Roy. Soc., A*, 1939, **170**, 145, 165; Levine and Dube, *Trans. Faraday Soc.*, 1939, **35**, 1125.

<sup>2</sup> Hamaker, *Rec. Trav. chim. Pays-Bas*, 1936, **55**, 1015; 1937, **56**, 1, 727; 1938, **57**, 61; *Physica*, 1937, **4**, 1058; *Symposium on Hydrophobic Colloids*, Ned. Chem. Vereen., Nov., 1937.

## 2. Properties of Energy at Contact.

We shall denote the electrical energy (first approximation) simply by  $F$  and the van der Waals energy by  $V$ . Then the total energy reads\*

$$E = F + V = (Q^2/Da)f_1(s, \tau) + Ag(s, a) \quad (1)$$

$$= \zeta^2 Da(1 + \tau)^2 f_1(s, \tau) + Ag(s, a), \quad (2)$$

where  $\tau = \kappa a$ ,  $D$  is the dielectric constant of the solution,  $s = R/a$  where  $R$  is the distance between the two particles, and

$$\zeta = Q/Da(1 + \tau). \quad (3)$$

The function  $f_1(s, \tau)$  has already been studied in the earlier papers<sup>3</sup> and for the van der Waals function we shall take the form given by Hamaker

$$g(s, a) = g(x) = -\frac{1}{12} \left\{ 2 \ln \frac{x(x+2)}{(x+1)^2} + \frac{1}{x(x+2)} + \frac{1}{(x+1)^2} \right\}, \quad (4)$$

where<sup>4</sup>

$$x = \frac{d}{2(a-\epsilon)} = \frac{R-2a+2\epsilon}{2(a-\epsilon)} = \left( \frac{1+u}{2} \right) s - 1$$

$$\text{or } s = \frac{2(1+x)}{1+u}, \quad u = \frac{\epsilon/a}{1-\epsilon/a}, \quad (5)$$

$d$  being the nearest distance between the centres of two surface atoms of the particles,  $\epsilon$  a quantity of the order of magnitude of the radius of an atom in the particle or in the water (we shall assume  $\epsilon = 1.5 \times 10^{-8}$  cm.) and  $A$  the van der Waals constant whose form has already been discussed by Hamaker. When  $s = 2$ , then for  $\tau \ll 1$ ,

$$f_1(2, \tau) = \frac{1}{2}(1 - 3\tau + \dots)$$

and for  $\tau \gg 1$ ,  $f_1(2, \tau) = 1/16\tau^2(1 + 7/2\tau + \dots)$ . Also we may write

$$g(2, a) = -(a/24\epsilon)(1 - \eta(\epsilon/a)), \quad (6)$$

where  $0 < \eta(\epsilon/a) < 1$  and  $\eta(\epsilon/a) \rightarrow 0$  as  $\epsilon/a \rightarrow 0$ .

It is convenient to introduce other units for  $Q$  and  $\zeta$ . We take  $Q_0 = 50e$  where  $e = 4.80 \times 10^{-10}$  e.s.u. is the electronic charge,  $D_0 = 80$ ,  $a_0 = 10^{-8}$  cm. and  $kT_0 = 4 \times 10^{-14}$  ergs where  $k$  is Boltzmann's constant and  $T_0$  is the temperature. Then  $Q_0^2/D_0a_0 = 180 kT_0$  and we shall introduce

$$Y = (Q/Q_0)(D_0a_0/Da)^{\frac{1}{2}} = \zeta(1 + \tau)(Da/180kT_0)^{\frac{1}{2}}, \quad (7)$$

making use of (3).

\* We should also include the repulsive short range exchange forces, which would lead to a minimum in the energy very close to contact. However, these forces will be simply represented by an impenetrable wall. We have also neglected the hydration and electrostrictive effects.

<sup>3</sup> We have omitted in this report certain properties of  $f(s, \tau)$  and  $g(x)$ , which facilitate the drawing of the curves in Figs. 1-5 and shall return to these in another paper dealing with further applications.

<sup>4</sup> Hamaker puts  $x = d/2a$  so that  $x = (s-2)/2 + u'$ ,  $u' = \epsilon/a$ . Actually, in order that the van der Waals energy be finite when the particles are touching, it is necessary that the radius of the spheres, in which Hamaker has assumed a uniform density of atoms, be less than  $a$ . However, the difference between the two forms for  $x$  is quite trivial particularly for  $a \gg \epsilon$  (other factors such as irregular particle surface are far more important). Either definition leads to practically the same curves in Figs. 1-5.

We first consider a monodisperse sol and examine the variation of the energy at contact  $E_{\text{con.}} = F_{\text{con.}} + V_{\text{con.}}$  with  $Q$  and  $\gamma$ . This is most readily shown by drawing constant  $F_{\text{con.}}$  curves in the plane ( $Y - \tau$ ). From (1) we obtain

$$v = F_{\text{con.}}/kT_0 = 180 Y^2 f_1(2, \tau) \quad \text{or} \quad Y = 0.0745 \{v/f_1(2, \tau)\}^{\frac{1}{2}}, \quad (8)$$

on substituting (7). When  $\tau \ll 1$ , (8) reduces to  $Y = 0.105v^{\frac{1}{2}}$  and when  $\tau \gg 1$  to  $Y = 0.298v^{\frac{1}{2}}\tau$ . When  $Y = 0$ , then necessarily  $v = 0$  for all  $\tau$ . In Fig. 1 we have plotted (8) in the ( $Y - \tau$ ) plane for various values of  $v$ . For the same sol  $V_{\text{con.}}$  will simply be a constant and hence a typical curve in Fig. 1 representing  $F_{\text{con.}} = vkT_0$  will also represent a constant value of  $E_{\text{con.}}$ , namely,  $E_{\text{con.}} = V_{\text{con.}} + vkT_0$ . Although  $F_{\text{con.}}$  is never negative,  $E_{\text{con.}} < 0$  when  $F_{\text{con.}} < -V_{\text{con.}}$  and the particular curve  $F_{\text{con.}} = -V_{\text{con.}}$  ( $E_{\text{con.}} = 0$ ) is such that all points in the ( $Y - \tau$ ) plane below this curve will correspond to negative  $E_{\text{con.}}$  and all points above to positive  $E_{\text{con.}}$ . If we add electrolyte to the given sol, *i.e.* increase  $\tau$ , then we describe some path in the ( $Y - \tau$ ) plane. To illustrate possible paths, we shall consider a sol with  $u = 0.01$  so that  $a = 1.5 \times 10^{-6}$  cm., at  $T = 18^\circ$  C. ( $D = 81$ ) and we shall add 1-1, 2-1 and 3-1 valency electrolyte types with  $\zeta$  decreasing from 60 m.v. to 45 m.v. for the first type and from 60 m.v. to 25 m.v. (critical potential) for the other two types. We have that  $\tau = \tau_1 = a\sqrt{\gamma}/3.04 \times 10^{-8}$  for the 1-1 case,  $\tau_2 = \sqrt{3}\tau_1$  for the 2-1 case and  $\tau_3 = \sqrt{6}\tau_1$  for the 3-1 case. Assuming that the precipitation values of the three types of electrolytes are  $\gamma_1^c = 4 \times 10^{-2}$ ,  $\gamma_2^c = 10^{-3}$  and  $\gamma_3^c = 10^{-4}$  mol./l., then  $\tau_1^c = 10$ ,  $\tau_2^c = 2.7$  and  $\tau_3^c = 1.2$ . Using (7) and (8) the corresponding values of  $Y$  and  $v$  are  $Y_1^c = 6.8$ ,  $Y_2^c = 1.3$  and  $Y_3^c = 0.76$  and  $v_1^c = 6.6$ ,  $v_2^c = 3.6$  and  $v_3^c = 5.2$  respectively at the critical coagulation points. If we assume, for simplicity, that the change in  $Y$  (or  $Q$ ) with addition of electrolyte is proportional to  $\tau$  (*i.e.* to  $\sqrt{\gamma}$ ) then the three paths illustrating the cases just described will be straight lines as shown in Fig. 1. Their equations are readily seen to be

$$Y_1 = 0.83 + 0.60 \tau_1, \quad Y_2 = 0.83 + 0.17 \tau_2 \quad \text{and} \quad Y_3 = 0.83 - 0.051 \tau_3.$$

Further, if we take  $A = kT_0$ , then  $V_{\text{con.}} = kT_0 g(0.01) = -3.6 kT_0$  and hence at the precipitation points  $E_{\text{con.}} = (v^c - 3.6) kT_0 = 3.0 kT_0, 0.0 kT_0$  and  $1.6 kT_0$  for the three cases. The curve  $E_{\text{con.}} = 0$  ( $v = 3.6$ ) is also shown in Fig. 1. We shall discuss the significance of these examples when we deal with the energy maximum in the next section.\*

In a similar fashion, we could examine the variation of  $F_{\text{con.}}$  with  $\zeta$  and  $\tau$  and also with the mobility and  $\tau$ . Whereas in Fig. 1, we find that as  $\tau$  increases at fixed  $Y$  (charge),  $F_{\text{con.}}$  ( $E_{\text{con.}}$ ) decreases very rapidly, we shall find that in the ( $\zeta - \tau$ ) plane, the tendency for  $F_{\text{con.}}$  ( $E_{\text{con.}}$ ) to diminish with increasing is much less marked and indeed at large  $\tau$  (large  $\gamma$  or  $a$ )  $F_{\text{con.}}$  is practically a function of  $\zeta$  only. Lack of space prevents us from examining this property in more detail.

In order to study the variation of  $E_{\text{con.}}$  with  $a$  it is instructive to draw energy contours in the ( $\kappa - a$ ) plane. The difficulty here is that the

\* The purpose of this illustration, both in Figs. 1 and 4, is to point out that at coagulation,  $E_{\text{max.}}$  (and  $E_{\text{con.}}$ ) are all of the same order of magnitude for different coagulating electrolytes. The initial value 60 m.v. for the  $\zeta$  potential, prior to the addition of the electrolyte, can certainly be replaced by a much higher one, if so required, without affecting the general argument.

dependence of  $Q$  ( $\zeta$ ) on  $\kappa$  and  $a$  is not satisfactorily known. Consequently we shall choose this dependence in a simple manner which at the same time roughly conforms with experiment. It will be assumed that  $\zeta$  is independent of  $a$  and also that  $Q$  is independent of  $\kappa$ , i.e. there is no particle adsorption of ions on addition of electrolyte.<sup>5</sup> Choosing  $Q = 50e$  when  $a = 10^{-6}$  cm., (3) yields

$$\zeta = 3 \times 10^{-4} / (1 + \kappa \cdot 10^{-6}) \text{ e.s.u.} = 90 / (1 + \kappa \cdot 10^{-6}) \text{ m.v.} \quad (9)$$

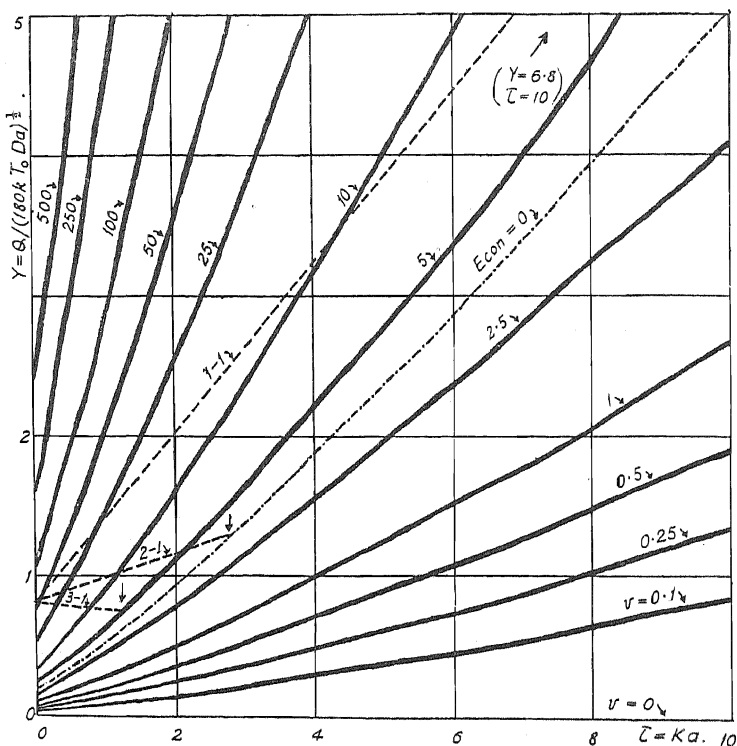


FIG. 1.—Energy at contact in  $(Y - \tau)$  plane, i.e. particle charge-electrolyte concentration plane. Contours represent constant values of  $v = F_{\text{con.}}/kT_0$ . Broken lines show the paths of the 1-1, 2-1, and 3-1 valency electrolyte types, the arrows marking critical precipitation points.

Putting  $A = 5 \times 10^{-14}$  and  $E_{\text{con.}} = w k T_0$  and substituting (6) and (9) in (2), we obtain

$$(1 + \kappa a)^2 f_1(2, \kappa a) = (1 + \kappa \cdot 10^{-6})^2 \left\{ 5.55 \times 10^{-9} \frac{w}{a} + 0.0193(1 - \eta(\epsilon/a)) \right\} \quad (10)$$

<sup>5</sup> According to the path of the 1-1 type in Fig. 1,  $Q$  definitely increases with  $\kappa$  and in many cases it seems nearer the truth to assume that  $\zeta$  is independent of  $\kappa$  for 1-1 electrolytes. According to Abramson, *Electrokinetic Phenomena*, American Chemical Society, Monograph Series, there is a rapid increase in charge with the addition of electrolyte, a limiting value being reached at about  $10^{-2}$  mol./l. beyond which  $Q$  is constant. For the 2-1 and 3-1 types in Fig. 1,  $Q$  is more nearly constant. If we assumed, for example, that  $\zeta$  is independent of both  $a$  and  $\kappa$  then the general features of the energy contours in Fig. 2 would not change. In the region  $E_{\text{con.}} > 0$ ,  $E_{\text{con.}}$  would still pass through a maximum and actually the curve  $E_{\text{con.}} = 0$  would be represented by one of the paths  $Z = \text{constant}$  in Fig. 3, which are similar to curve A.

In Fig. 2 the relation (10) is plotted in the  $\kappa$ - $a$  plane (or equivalently in the  $\zeta$ - $a$  plane) for various values of  $w$ . It has already been proved<sup>1</sup> that for every  $\kappa$ , a value of the radius can be found such that  $E_{\text{con.}} = 0$  ( $w = 0$ ) provided  $D/2 \geq (A/24\epsilon\zeta^2)(1 - \eta(\epsilon/a)) \geq D/16$ , which becomes  $25.9 \geq (1 + \kappa \cdot 10^{-6})^2(1 - \eta(\epsilon/a)) \geq 3.24$  in the particular case considered here. Otherwise  $E_{\text{con.}} \geq 0$  for all  $a$  according as  $(1 + \kappa \cdot 10^{-6})^2(1 - \eta(\epsilon/a)) > 3.24$  or  $< 25.9$ . In Fig. 2 this implies that  $E_{\text{con.}} > 0$  for all  $a$  if  $\kappa < 0.8 \times 10^6$ . We also proved that for fixed  $\kappa$  (or  $\zeta$ ), as we increase  $a$  from very small values (the range  $a < 10^{-7}$  cm. may be ignored), then in the region where  $E_{\text{con.}} > 0$ ,  $E_{\text{con.}}$  at first in-

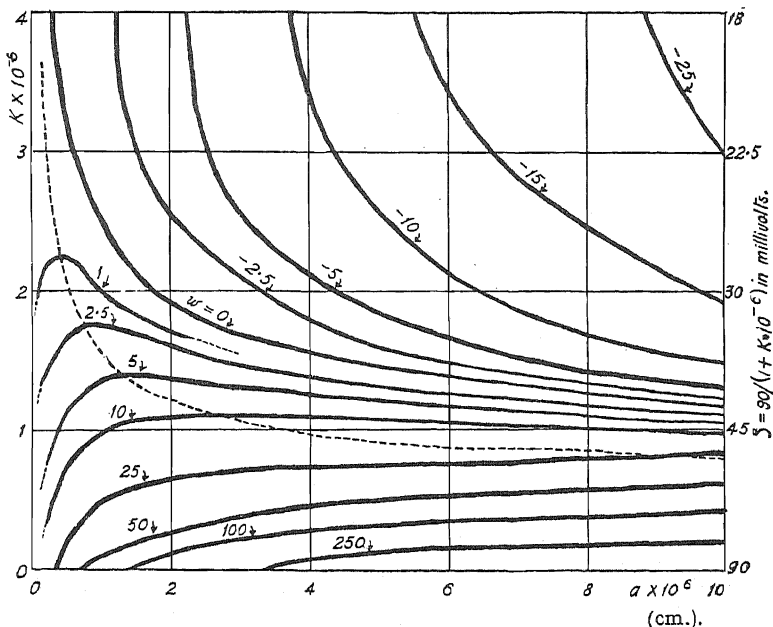


FIG. 2.—Energy at contact in the  $(\kappa - a)$  plane, *i.e.* in particle radius-electrolyte concentration plane or equivalently in particle radius- $\zeta$  potential plane. Contours represent constant values of  $w = E_{\text{con.}}/kT_0$  for a sol in which  $\zeta$  is independent of the radius and there is no adsorption of charge on addition of electrolyte. Broken curve shows path of maximum.

creases, reaching a maximum and then decreases again. The path of this maximum is indicated in Fig. 2, its equation being

$$\frac{d}{d\tau} \{ \tau(1 + \tau)^2 f_1(2, \tau) \} = 0.462(1 + \kappa \cdot 10^{-6})^2 u^2 \frac{dg(u)}{du}. \quad (11)$$

Now  $E_{\text{max.}}$ , the energy at the maximum, is the controlling factor in stability but we shall see in the next section that  $E_{\text{con.}}$  behaves similarly to  $E_{\text{max.}}$ , the chief difference being that  $E_{\text{con.}} \leq E_{\text{max.}}$  so that when plotting  $E_{\text{max.}}$  in the  $(\kappa - a)$  plane the energy curves will be shifted towards larger values of  $\kappa$  relative to the plot of  $E_{\text{con.}}$ . Consequently we shall assume that Fig. 2 qualitatively represents the variation of  $E_{\text{max.}}$  in the  $(\kappa - a)$  plane. In the region  $E_{\text{con.}} > 0$ , it is noticed that at any given  $\kappa$  (electrolyte concentration) there is a wide range of values for the particle radius, over which the sol will be stable. It is true that a maximum stability appears to exist but provided  $a$  is not too small

it is not pronounced. Indeed, provided  $\kappa < 0.8 \times 10^6$  (*circa*) in our case <sup>6</sup> there is no upper limit to the particle radius (*i.e.* provided  $\zeta > 50$  m.v. according to (9)). Thus our results do not lead to the erroneous conclusions reached by others <sup>7</sup> that particles of a definite size or in a definite range only can exist.

A few preliminary remarks will be made on the significance of the maximum. At very small radii ( $a \sim 10^{-7}$  cm.),  $E_{\text{con.}}$  definitely decreases even for small  $\kappa$  (small  $\gamma$  or large  $\zeta$ ). This is in accordance with the fact that there is a lower range of size for colloidal particles. Further, the maximum is probably related to the possible formation of secondary particles from primary ones, to the aging process and similar phenomena. Gyemant <sup>8</sup> has attempted to explain the distribution of size in poly-disperse sols along such lines using a crude expression for the mutual energy. We believe that the application of our results in this direction should yield more satisfactory information concerning the rôle played by aggregation in the growth and size distribution of particles.

The behaviour of  $E_{\text{con.}}$  (or  $E_{\text{max.}}$ ) in the region where it is negative (*i.e.* for larger electrolyte concentrations, in the range of coagulation) suggests that at the same value of  $\kappa$  (or  $\zeta$ ) the stability decreases with increasing particle size (since in Fig. 2, for fixed  $\kappa$ , in the region  $E_{\text{con.}} < 0$ ,  $E_{\text{con.}}$  diminishes with increasing radius, *i.e.* becomes a larger negative quantity). This is in agreement with experiment. Thus, Tuorila <sup>9</sup> reported that small gold particles coagulate more slowly than the larger ones (under the same conditions). Further, this explains the phenomena of stepwise coagulation,<sup>10</sup> where the largest particles precipitate first, followed by the smaller ones in order of decreasing size.

It is instructive to examine the behaviour of the condition  $E_{\text{con.}} = 0$  or

$$Z = 10^{-7} D \zeta^2 / A = (1 - \eta(\epsilon/a)) / \{3.6(1 + \tau)^2 f_1(2, \tau)\}, \quad (12)$$

from (2) and (6). When  $\tau \ll 1$ , this reduces to  $Z' = (1 - \eta(\epsilon/a)) / 1.8$ , and when  $\tau \gg 1$  to  $Z'' = 4.4(1 - \eta(\epsilon/a))$ . Equation (12) has been plotted in Fig. 3 in the  $(\kappa - a)$  plane for various  $Z$ . From (12) it follows

<sup>6</sup> If we consider a second example, namely a 1-1 type of electrolyte for which  $\zeta = 45$  m.v. is constant, independent of  $\kappa$  and  $a$ , then in the plot of  $E_{\text{con.}}$  in the  $(\kappa - a)$  plane, the curve  $E_{\text{con.}} = 0$  would be that given by  $Z = 3.6$  in Fig. 3. In this case, particles of radii less than  $10^{-6}$  cm. would be stable provided  $\kappa < 3 \times 10^6$  or  $\zeta > 22.5$  m.v. From the form of curve  $A$  in Fig. 5, representing the path of the condition  $E_{\text{max.}} = 0$ , which should be considered rather than  $A$  in Fig. 3 (and 2), the bounds  $\kappa < 0.8 \times 10^6$ ,  $\zeta > 50$  m.v. should really be replaced by  $\kappa < 1.3 \times 10^6$ ,  $\zeta > 39$  m.v. (*circa*) for particles less than  $10^{-6}$  cm. in radius. The second example mentioned in this footnote yields practically the same paths for  $E_{\text{max.}}$  and  $E_{\text{con.}}$  so that its bounds are not changed appreciably. Only the order of magnitude of the lower bounds for  $\zeta$  quoted here are significant. Their exact values depend on  $A$  and also increase with diminishing  $a$ .

<sup>7</sup> Rice, *J. Physic. Chem.*, 1926, **30**, 189. Gyemant, *Grundzuge der Kolloid Physik*, 1927, 43, Sammlung, Vieweg; Volmer, *Z. physik. chem.*, 1927, **125**, 151; March, *Ann. Physik*, 1927, **84**, 605; *Koll. Z.*, 1928, **45**, 97.

<sup>8</sup> Gyemant, *Z. Physik*, 1926, **36**, 457.

<sup>9</sup> Tuorila, *Koll. Beih.*, 1926, **22**, 282; see *ibid.*, 1928, **27**, 180 for earlier references.

<sup>10</sup> Cf. Weiser, *Inorgan. Coll. Chem.*, vol. i., p. 321, 1933; vol. iii., p. 85, 1938, Wiley & Sons. In addition, our theory predicts that the critical  $\zeta$  potential increases with particle size, in agreement with experiment, since in stepwise coagulation, the larger particles coming out first have a higher potential than the smaller ones which coagulate later. Recently, Derjaguin, *Acta Physico-chimica*, U.S.S.R., 1939, **10**, 333, who attempts to derive the potential energy of two spherical particles by transferring expressions developed for two parallel plates, came to the opposite conclusion as a result of his omission of the van der Waals energy of attraction.

that  $E_{\text{con.}} < 0$  or  $> 0$  for all  $\kappa$  according as  $Z < Z'$  or  $Z > Z''$ . In Fig. 3 we have represented by  $A$  the curve obtained by putting  $w = 0$  in (10), to which the following interpretation can be given. Curve  $A$  gives the conditions under which the energy value  $E_{\text{con.}} = 0$  is reached by a polydisperse sol in which (i) all the particles have the same  $\zeta$  potential given by (9), (ii) the charge on the particles does not change with the addition of electrolyte. We see that as  $\kappa$  increases (electrolyte added) the largest particles reach  $E_{\text{con.}} = 0$  first and then the smaller ones. For particles of a given radius  $a_1$  at a specified electrolyte concentration ( $\kappa_1$ ) the value of  $Z_1$  (i.e. of  $\zeta_1$ ) at which  $E_{\text{con.}} = 0$  is given by the particular curve passing through the point  $(\kappa_1, a_1)$ . If we con-

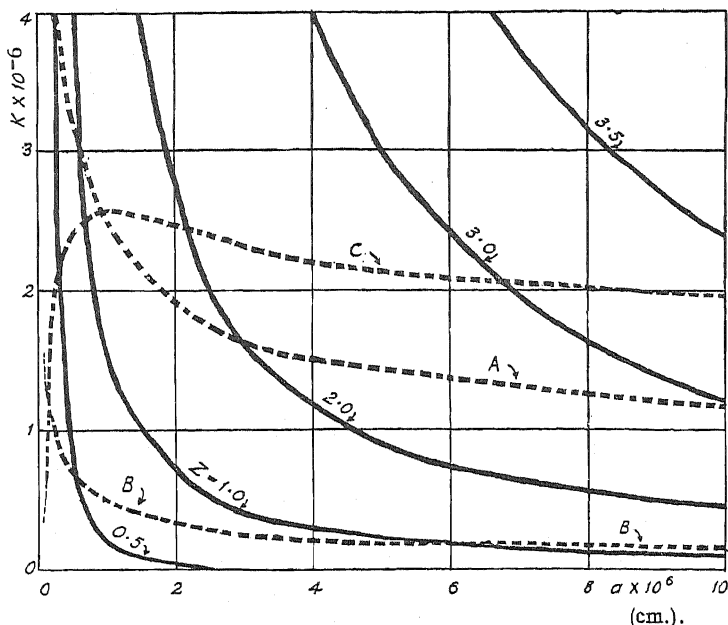


FIG. 3.—Representation of condition that energy at contact is zero in the  $(\kappa - a)$  plane. Contours represent constant values of  $Z = 10^{-7} D\zeta^2/A$ , i.e. constant  $\zeta$  potentials. Broken curves show paths of actual types of polydisperse sols,  $A$  and  $B$  describing sols with the same properties as those in Fig. 2 and  $C$  describing sols whose particles have fixed charge per unit surface area.

sider another sol with a rather high van der Waals' energy, say  $A = 5 \times 10^{-13}$ , then we get curve  $B$ . On replacing  $0.0193$  by  $0.193$  and putting  $u = 0$  in (10) it is readily seen for large  $a$  and small  $\kappa$ ,  $B$  is represented by  $\kappa a \approx 2$ , i.e.  $B$  approaches the  $a$  axis asymptotically. Instead of assuming that  $\zeta$  is independent of  $a$ , we can also examine the condition that the charge per unit area of particle surface is constant, say  $Q/a^2 = 50e/(10^{-6})^2 = 2.4 \times 10^4$  e.s.u., the charge being independent of  $\kappa$ . The path of the condition  $E_{\text{con.}} = 0$  for this type of polydisperse sol is shown by curve  $C$  in Fig. 3 and is obtained in a similar fashion to  $A$  and  $B$ .<sup>11</sup>

<sup>11</sup> The equations of curves  $A$ ,  $B$  and  $C$  are  $Z = 14.4/(1 + \kappa \cdot 10^{-6})^2$ ,  $Z = 1.44/(1 + \kappa \cdot 10^{-6})^2$ ,  $Z = 1.44 \times 10^{13} a^2 / (1 + \kappa a)^2$  respectively, making use of (3) and (12).



### 3. Properties of Energy Maximum.

In one of the earlier papers we only indicated the presence of the maximum  $E_{\max.}$  but since it is the controlling factor with respect to the stability properties of the sol it is important to study its behaviour in more detail. The position of the maximum

$$s_{\max.} = R_{\max.}/a = s_m = 2(1 + x_m)/(1 + u),$$

for brevity, is given by the relation  $dE/ds = 0$ , yielding

$$y^2 = -g'(s_m, a)/180 f_1'(s_m, \tau), \quad g'(s_m, a) = (1 + u)g'(x_m)/2, \quad (13)$$

using (1) and putting  $g'(s, a) = dg(s, a)/ds$ ,  $f_1'(s, \tau) = df_1(s, \tau)/ds$ ,  $g'(x) = dg(x)/dx$ ,  $y = Y(kT_0/A)^{1/2}$ . It has been found convenient to combine  $Y$  (or the charge  $Q$ ) and the van der Waals constant  $A$  into one variable. It follows that

$$s_m = s_m(y, \tau, a) \quad . \quad . \quad . \quad (14)$$

$$\text{and} \quad U_{\max.} = E_{\max.}/A = 180y^2 f_1(s_m, \tau) + g(s_m, a). \quad (15)$$

We shall first investigate the necessary condition for the existence of the maximum. Since  $E_{\text{con.}} \leq E_{\max.}$ , such a condition is that  $dE/ds \geq 0$  at contact ( $s = 2$ ), i.e. according to (1) and (2)

$$\frac{10^{-16} Q^2}{ADa^3} \leq \frac{1 - h(\epsilon/a)}{27(1 - p(\tau))} \quad \text{or} \quad \frac{10^{-16} \zeta^2 D}{Aa} \leq \frac{1 - h(\epsilon/a)}{27(1 + \tau)^2(1 - p(\tau))}, \quad (16)$$

where  $g'(2, a) = (1/48)(a/\epsilon)^2(1 - h(\epsilon/a))$ ,  $0 \leq h(\epsilon/a) \leq 1$ ,  $h(\epsilon/a) \rightarrow 0$  as  $a \rightarrow \infty$ ;  $f_1'(2, \tau) = -(1/4)(1 - p(\tau))$ ,  $0 \leq p(\tau) < 1$ ,  $p(\tau) \rightarrow 0$  as  $\tau \rightarrow 0$ ;  $\epsilon = 1.5 \times 10^{-8}$  cm. If  $Q$  or  $\zeta$  is so large that (16) is not satisfied then the particles repel one another right up to contact position. An indication of the condition for peptisation can be obtained from (16) although strictly we really require the energy associated with a number of particles in close contact in the sediment. Peptisation will be possible provided  $E_{\max.} - E_{\text{con.}} \sim kT$ . A more stringent condition is  $dE/ds \leq 0$ . Since peptisation usually occurs at very small electrolyte concentrations we shall put  $\tau = 0$  so that the latter condition becomes

$$\frac{10^{-16} Q^2}{ADa^3} \geq \frac{1}{27}(1 - h(\epsilon/a)) \quad \text{or} \quad \frac{10^{-16} \zeta^2 D}{Aa} \geq \frac{1}{27}(1 - h(\epsilon/a)). \quad (17)$$

If  $\zeta$  is assumed to be the same for particles of different radii in the sediment, then as we increase  $\zeta$  (e.g. by washing) the smaller particles will reach the condition (17) first and hence return to the sol state, in agreement with experiment since small particles are more easily peptised than large ones. It is readily seen that, if the charge per unit area is assumed constant, then the larger particles will be peptised first, so that this latter condition is not in accord with experiment.

Again we shall consider a monodisperse sol and study the variation of  $E_{\max.}$  (and  $s_m$ ) with  $Q$  and  $\gamma$ , proceeding in the following manner. The value  $u = 0.01$  ( $a = 1.5 \times 10^{-6}$  cm.) is again chosen. We wish to separate the dependence on  $\tau$  and  $a$  as much as possible to facilitate the computations. On putting  $\tau = 0$  (13) and (15) reduce to

$$y_0^2 = s_m^2 g'(s_m, a)/180 = (1 + x_m)^2 g'(x_m)/90(1 + u), \quad (18)$$

$$U_{\max.}^0 = s_m g'(s_m, a) + g(s_m, a) = (1 + x_m)g'(x_m) + g(x_m), \quad (19)$$

and we can now write (13) and (15) as

$$y^2 = -y_0^2/s_m^2 f_1'(s_m, \tau),$$

$$U_m - U_m^0 = - (180 y_0^2/s_m^2) \{f_1(s_m, \tau)/f_1'(s_m, \tau) + s_m\}. \quad (20)$$

We now plot contours in the  $y - \tau$  plane representing constant values of  $U_{\max.}$  and  $s_m$  (Fig. 4). To do so, values of  $x_m$  (or  $s_m$ ) are chosen and  $U_{\max.}^0$  and  $y_0$  are determined as functions of  $x_m$ . For fixed  $u$  (or  $a$ ),  $U_{\max.}^0$

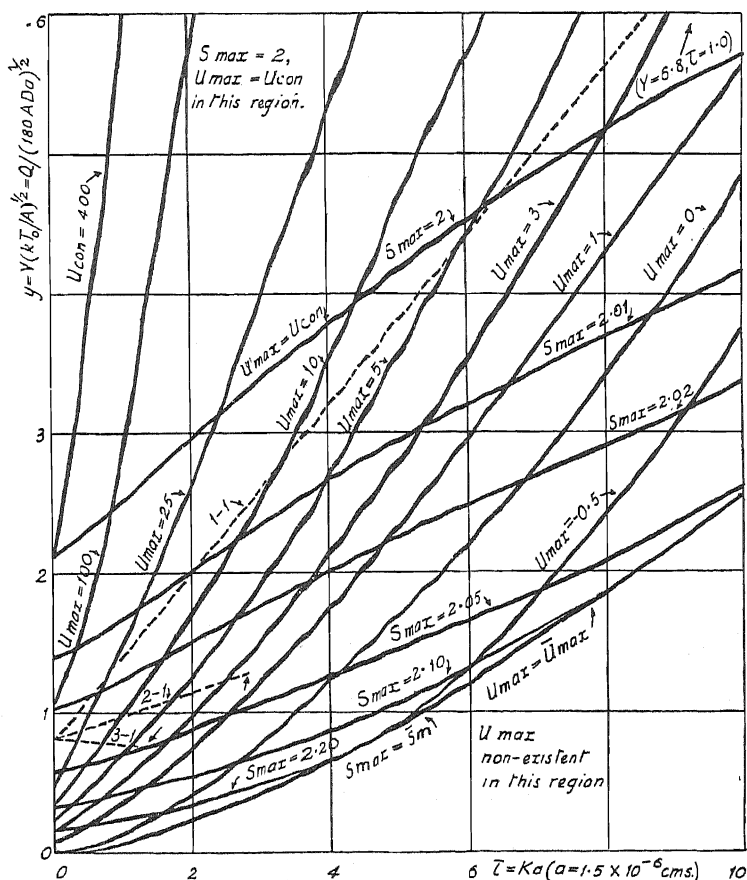


FIG. 4.—Energy maximum in the  $(y - \tau)$  plane, i.e. in particle-charge-electrolyte concentration plane. One set of contours represents constant values of  $U_{\max.}$  the other of  $s_{\max.}$  ( $= s_m$ ). Broken lines show path of same electrolytes as in Fig. 1.

is a function of  $y_0$  only since  $x_m$  can be eliminated from (18) and (19). Then choosing a value of  $\tau$ , we calculate  $y$  and  $U_{\max.}$  from (20) as a function of  $x_m$  (or  $s_m$ ). Thus for each  $\tau$ , (20) may be written as  $y = y(s_m)$ ,  $U_{\max.} = U_{\max.}(s_m)$ . On eliminating  $s_m$ , this yields  $U_{\max.} = U_{\max.}(y)$  and inverting the first relation we derive  $s_m = s_m(y)$ , for given  $\tau$ . In this way we can compute the functions  $U_{\max.} = U_{\max.}(y, \tau)$  and  $s_m = s_m(y, \tau)$  and so obtain Fig. 4. In the actual numerical calculations free use is made of interpolation.

When  $(dE/ds)_{s=2} \leq 0$ , then  $E_{\max.} = E_{\text{con.}}$  and  $s_m = 2$  since the maximum disappears. The condition  $(dE/ds)_{s=2} = 0$  may be written as  $y^2 = -1.12/f_1'(2, \tau)$  putting  $s_m = 2$  in (13) so that, according to (5)  $x_m = u = 0.01$ . In Fig. 4 this forms the boundary line such that below it  $U_{\max.}$  (or  $E_{\max.}$ ) exists and above it  $U_{\max.} = U_{\text{con.}} = E_{\text{con.}}/A$  and  $s_m = 2$ . The value of  $U_{\max.}$  along this dividing line is

$$U_{\max.} = U_{\text{con.}} = 180y^2f_1(2, \tau) - g(0.01) = -202f_1(2, \tau)/f_1'(2, \tau) - 3.6, \quad (21)$$

using (13) and (15). When  $\tau \ll 1$ , we get  $y^2 = 4.5$  and  $U_{\max.} = 400$  and when  $\tau \gg 1$ ,  $y^2 = 3\tau$  and  $U_{\max.} = 34/\tau$ . Above the line we may write (21) as  $y = 0.0745 \{U_{\text{con.}} + 3.6/f_1(2, \tau)\}^{1/2}$  similar to (8).

The curves for  $U_{\max.}$  in Fig. 4 are seen to behave quite similarly to those of  $E_{\text{con.}}$  (or  $F_{\text{con.}}$ ) in Fig. 1. The condition  $U_{\max.} = 0$  is not given by  $y = 0$  but by

$$y^2 = -g'(s_m, a)/180f_1'(s_m, \tau) = -g(s_m, a)/180f_1(s_m, \tau), \quad (22)$$

as obtained from (13) and (15). This represents the relation between  $y$  and  $\tau$  (for given  $a$ ) in terms of the parameter  $s_m$  and is shown in Fig. 4. The region  $U_{\max.} < 0$  does not extend to  $y = 0$  but is bounded by another curve obtained in the following manner. From Fig. 4 it is seen that as we decrease  $y$ ,  $s_m$  increases, i.e. the maximum moves out,  $\tau$  being kept constant. According to (13), this implies that  $g'(s_m, a)$  decreases more rapidly than  $f_1'(s_m, \tau)$  with increase in  $s_m$  (for given  $\tau$  (or  $\kappa$ ) and  $a$ ). However, at the minimum  $s = s_{\min.}$  of  $f_1(s, \tau)$ ,  $f_1'(s_{\min.}, \tau) = 0$  where (13) yields an infinite value for  $y$ . It follows that the above diminution in  $y$  with increasing  $s_m$  must stop at a certain value  $s_m = \bar{s}_m$  where  $y$  reaches a minimum  $\bar{y}$ , say, and for further increase in  $s_m$ ,  $y$  must also increase tending to infinity as  $s_m \rightarrow s_{\min.}$  The value  $\bar{s}_m$  is given by  $(\partial y/\partial s_m)_{s_m=\bar{s}_m} = 0$  (partial differentiation to denote that  $\tau$  and  $a$  are fixed) so that  $\bar{s}_m = \bar{s}_m(\tau, a)$ ,  $\bar{y} = y(\bar{s}_m, \tau, a)$  and  $\bar{U}_{\max.} = U_{\max.}(\bar{y}, \bar{s}_m, \tau, a)$  are functions of  $\tau$  and  $a$ . It is readily seen from (13) and (15) that this latter condition leads to  $(\partial^2 U_{\max.}/\partial s_m^2)_{s=\bar{s}_m} = 0$ . In Fig. 4 this lower limit has been plotted (approximately only, in view of the tedious numerical work). The region  $\bar{s}_m \leq s_m \leq s_{\min.}$  can be shown to refer to the minimum in the mutual energy of the two particles and this will be discussed in a further paper.

In order to discuss the application of Fig. 4 to stability properties, we should first mention the theory of slow coagulation developed by Fuchs<sup>12</sup> taking into account the repulsive forces between the colloidal particles (aerosol in the case treated by Fuchs). Adopting his method and assuming that secondary particles are formed from collisions of primary particles once they pass over the energy barrier  $E_{\max.}$ , we find that the specific coagulation time is given by

$$\theta = \{1 - \chi(y, \tau, a)\} e^{E_{\max.}/kT} / 4\pi D R_{\max.} n, \quad (23)$$

where  $n$  is the number of particles per unit volume and  $0 < \chi < 1$ . For  $E_{\max.} \gg kT$ ,  $\chi$  is of the form  $s_m/s^*$  with  $s_m < s^* < s_{\min.}$  and for

$|E| \ll kT$ ,  $\chi \ll 1$  so that we obtain the original Smoluchowski formula (strictly  $R_{\max.}$  should be replaced by  $2a$  (to  $3a$ ) in the latter case). The above formula is based on the assumption that if  $\theta/2$  is the coagulation time associated with the formation of secondary particles from primary ones, then  $\theta$  is that describing the formation of all types of multiple

<sup>12</sup> Fuchs, *Z. physik.*, 1934, 89, 735.

particles, the quantity that is measured experimentally. The details concerning the exact form of  $\chi$  will be discussed elsewhere. The correction factor  $\xi$  for slow coagulation becomes

$$\ln \xi = \ln (\theta_{\text{slow}}/\theta_{\text{fast}}) \approx E_{\text{max.}}/kT + \ln (1 - \chi), \quad (24)$$

the first term being positive and the second negative. When  $E_{\text{max.}} \gg kT$  (very slow coagulation) and  $\tau$  small (range of the electrical repulsive forces large compared with  $a$ ), then the first term in (24) is the predominant one although it is likely that it will remain the more important even for large  $\tau$ . Thus we shall tentatively assume that  $E_{\text{max.}}$  is the chief controlling quantity determining stability.<sup>13</sup>

Again we draw the three paths illustrating the history of the sol on addition of a 1-1, 2-1 and 3-1 valency types of electrolytes already shown in Fig. 1. We notice that here the values of  $U_{\text{max.}}$  at the critical coagulation are <sup>14</sup> 3.0,  $\sim 2.0$  and  $\sim 4.0$  for the three cases which are in somewhat more satisfactory agreement than the values of  $E_{\text{con.}}$  We cannot expect that the values of  $U_{\text{max.}}$  (or  $E_{\text{max.}}$ ) should be exactly the same for the three cases since  $\chi$  will not be the same. Furthermore there will be a correction from the use of the complete Debye-Hückel equation, particularly for the 3-1 electrolyte.

The three paths illustrated merit close attention. They explain in a very clear fashion the long discussed problem as to why electrolytes which coagulate at high concentrations also have high critical potentials. In the 1-1 case, there is a constant increase in charge with addition of electrolyte (and consequently a rather slow drop in  $\zeta$ ) and as a result the value of  $U_{\text{max.}}$  (or  $E_{\text{max.}}$ ) decreases slowly so that we need to reach high electrolyte concentrations before precipitation begins. Further, coagulation sets in more gradually than in the 2-1 and 3-1 types. Strictly speaking there is no critical potential but rather a small range of electrolyte concentration where the coagulation passes from being extremely slow to rapid. On the other hand, for the 2-1 type there is comparatively little change in particle charge with addition of electrolyte and both  $U_{\text{max.}}$  and  $\zeta$  diminish more rapidly. For the 3-1 type the tendency for a diminution of charge and consequently for an even more rapid drop in  $U_{\text{max.}}$  and  $\zeta$  is greater.

We shall only examine the condition  $E_{\text{max.}} = 0$  in the  $(\kappa - a)$  plane corresponding to Fig. 3, and shown in Fig. 5. Using (2), we can write this condition in a form similar to (12), namely

$$\begin{aligned} 10^7 Z a &= \zeta^2 D a / A = -g'(s_m, a) / 180 (1 + \tau)^2 f_1'(s_m, \tau) \\ &= -g(s_m, a) / 180 (1 + \tau)^2 f_1(s_m, \tau), \end{aligned} \quad (26)$$

and corresponding to (22). To obtain the curves in Fig. 5, representing constant  $Z$  values in the  $(\kappa - a)$  plane, we first obtain  $s_m$  as a function of  $a$  and  $\kappa$  (or  $\tau$ ) from the second equation in (26) (identical with the second

<sup>13</sup> Cf. Derjaguin, *loc. cit.*,<sup>10</sup> who comes to the same conclusion. More recent calculations by us show that for large  $\tau$  ( $> 5$ ) and small  $E_{\text{max.}}$  ( $\sim kT_0$ ), the term  $\ln (1 - \chi)$  in (24) does become quite appreciable.

<sup>14</sup> The value of  $U_{\text{max.}}$  becomes 3.0 for the 2-1 electrolyte when the critical  $\zeta$  potential is changed from 25 to 27 m.v. It is noticed that for the 1-1 type,  $E_{\text{max.}} = E_{\text{con.}}$  at the coagulation point, *i.e.* the particles repel one another right up to contact. However, many corrections will have to be considered at such close distances, in particular our simple expression for the van der Waals energy is probably no longer sufficiently accurate. On the whole our results certainly give the right order of magnitude for  $E_{\text{max.}}$  ( $U_{\text{max.}}$ ) and indeed we could hardly expect better agreement with experiment in view of the approximations from the theoretical side.

equation in (22)), and then compute  $Z$  as a function of  $\kappa$  and  $a$ . It is found that for fixed  $a$ ,  $s_m$  decreases as  $\kappa$  increases, which is to be expected since the range of the electrical forces diminishes. When  $\tau \ll 1$  the values of  $s_m$  are quite large ( $s_m \rightarrow \infty$  as  $\tau \rightarrow 0$ ). From Fig. 5, we can find the  $\zeta$  potential at which rapid coagulation will take place provided we know the type of particle (*i.e.* the van der Waals constant  $A$ ), the radius of the particle and the electrolyte type and concentration. In a similar fashion we could predict the  $\zeta$  potential for various degrees of slow coagulation (including the critical potential) by drawing curves in the  $(\kappa-a)$  plane representing  $E_{\max.}$  as the appropriate small multiple of  $kT$  (corrected by the factor  $1 - \chi$  if necessary).

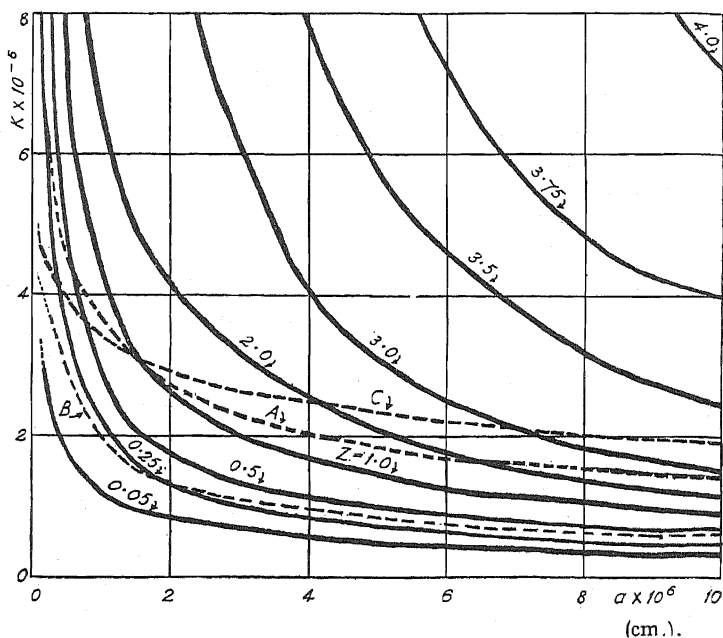


FIG. 5.—Representation of condition that energy maximum is zero in the  $(\kappa-a)$  plane. Contours represent same quantities ( $Z$ ) as in Fig. 3 and likewise the broken curves A, B and C. Actually the curves  $Z = 3.5$ ,  $3.75$  and  $4.0$  describe condition  $E_{\text{con.}} = 0$  since we assume  $E_{\max.} = E_{\text{con.}}$  for large  $\tau$  ( $> 25$ ). The true curves ( $E_{\max.} = 0$ ) may lie somewhat above these.

As an example, we have considered an AgI sol. Let  $q_p$  and  $q_w$  be the number of atoms per c.c. in the particle and water respectively,  $C_{pp}$ ,  $C_{pw}$  and  $C_{ww}$  the van der Waals constant (associated with the London dispersion forces) for the atom pairs particle-particle, particle-water, and water-water.<sup>15</sup> Then, according to Hamaker

$$A = \pi^2(q_p^2 C_{pp} + q_w^2 C_{ww} - 2q_p q_w C_{pw}). \quad (27)$$

<sup>15</sup> For two atoms 1 and 2, polarisabilities  $\alpha_1$  and  $\alpha_2$ , with  $n_1$  and  $n_2$  electrons in the outer shell, we shall use the formula

$$C_{12} = 22.5 \times 10^{-24} \alpha_1 \alpha_2 / \{(\alpha_1/n_1)^{\frac{1}{2}} + (\alpha_2/n_2)^{\frac{1}{2}}\}^2 \text{ c.g.s. units.}$$

Then in the above case (Ag and I referring to silver and iodine ions)

$$C_{22} = \frac{1}{2}(C_I, I + C_{Ag, Ag} + 2C_{Ag, I}), \quad C_{pw} = \frac{1}{2}(C_{Ag, w} + C_{I, w}).$$

Introducing the appropriate numerical values<sup>16</sup> for the various quantities in (27) for AgI particles we calculate  $q_p^2 C_{pp} + q_w^2 C_{ww} = 3.25 \times 10^{-13}$ ,  $2q_p q_w C_{pw} = 2.64 \times 10^{-13}$  and  $A = 6.0 \times 10^{-13}$ . Since we are subtracting two quantities of the same order and subject to some error (due to the unknown structure and shape of the particle surface which yields the greater contribution to  $A$ ), to obtain a much smaller resultant, we should not attach any importance to the exact numerical value of  $A$ .

When comparing with experiment, it is convenient to compute  $A$  rather than  $\zeta$ , using the relation (12) and the contours for  $Z$  (or  $\zeta$ ) in Fig. 5. Appealing to the measurements of Kruyt and van Gils<sup>17</sup> on the change in mobility of AgI sol with the addition of  $\text{KNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  we give the values of  $A$  in Table I as computed from their data. It is difficult to decide which points on their mobility curves in the coagulation zone correspond to the condition  $E_{\max.} = 0$ , and consequently we have chosen somewhat arbitrarily two points for each electrolyte. Particularly for  $\text{Al}(\text{NO}_3)_3$ ,  $E_{\max.}$  drops quite rapidly with a small increase in  $\kappa$  and the two values of  $A$  computed for this electrolyte differ considerably so that their significance is rather doubtful. However, the values of  $A$  for  $\text{KNO}_3$  and  $\text{Na}(\text{NO}_3)_2$  change less rapidly and we see that there is fair agreement among them. The fact that the values of  $A$  in Table I are much less than the supposedly theoretical one ( $6.0 \times 10^{-13}$ ) indicates to what extent  $A$  depends on the surface structure and shape of the particle.\*

We can again draw curves A, B and C in Fig. 5 just as in Fig. 3, making use of their equations given in footnote <sup>11</sup>. If we were to construct the curves for constant  $E_{\max.}$  in the  $(\kappa-a)$  plane, corresponding to the representation of  $E_{\text{con.}}$  in Fig. 3, then A in Fig. 5

TABLE I.

$a = 5 \times 10^{-8}$  cm.,  $T = 298^\circ$ ,  $D = 78.8$ ,  $\zeta = 4\pi\eta u/D$ ,  $u$  = mobility,  $\eta = 0.00895$  (viscosity of water).

Electrolyte.	$\gamma$ mol./l.	$u$ $\mu$ /sec.	$\zeta$ m.v.	$\kappa \times 10^{-6}$ .	$Z$ .	$A \times 10^{14}$ .
<b>First Set</b>						
$\text{KNO}_3$	$5 \times 10^{-2}$	2.5	36	7.4	3.6	2.8
$\text{Ba}(\text{NO}_3)_2$	$10^{-3}$	1.3	19	1.8	1.6	1.8
$\text{Al}(\text{NO}_3)_3$	$4 \times 10^{-5}$	0.4	6	0.51	0.05	5.7
<b>Second Set</b>						
$\text{KNO}_3$	$10^{-1}$	2.0	29	10	3.7	1.8
$\text{Ba}(\text{NO}_3)_2$	$3 \times 10^{-3}$	1.5	21	3.1	3.0	1.2
$\text{Al}(\text{NO}_3)_3$	$10^{-4}$	0.3	4	0.81	1.3	1.0

would be the path of  $E_{\max.} = 0$  and would play a similar rôle to the condition  $E_{\text{con.}} = 0$  in Fig. 3. Thus the region above A would correspond to  $E_{\max.} < 0$  and that below to  $E_{\max.} > 0$ . Although we cannot

<sup>16</sup>  $\alpha_w = 1.58 \times 10^{-24}$ ,  $\alpha_{\text{Ag}} = 1.72 \times 10^{-24}$ ,  $\alpha_{\text{I}} = 7.29 \times 10^{-24}$ ;  $n_w = n_{\text{I}} = 8$ ,  $n_{\text{Ag}} = 18$ ;  $C_{w,w} = 62.9 \times 10^{-60}$ ,  $C_{\text{Ag},w} = 81.2 \times 10^{-60}$ ,  $C_{\text{I},w} = 185 \times 10^{-60}$ ,  $C_{\text{Ag},\text{Ag}} = 108 \times 10^{-60}$ ,  $C_{\text{I},\text{I}} = 626 \times 10^{-60}$ ,  $C_{\text{Ag},\text{I}} = 223 \times 10^{-60}$ ,  $q_p = 2.93 \times 10^{22}$ ,  $q_w = 3.36 \times 10^{22}$ .

<sup>17</sup> Kruyt and van Gils, *Koll. Z.*, 1937, 78, 32. The values in Table I are taken from their graph, and are necessarily very rough.

\* Another interpretation is that the hydration and electrostrictive effects partly counteract the van der Waals attraction.

definitely say without further computations that in the latter region maxima analogous to those in Fig. 3 would exist, it seems likely that this will be so. Similar remarks can be made concerning B and C. We notice that although in Fig. 3, B cuts the ordinate  $a = 10^{-5}$  cm. at  $\kappa = 0.15 \times 10^6$  the corresponding value in Fig. 5 is  $\kappa = 0.6 \times 10^6$ , which supports our statement concerning the non-existence of any particular limit to the particle size.

The examples treated in this report should only be considered as a mere beginning of the applications that can be made of the mutual energy between colloidal particles. The usefulness of drawing constant energy curves to illustrate the various stability properties, as suggested by Hamaker, is worthy of attention. The fact that not only the  $\zeta$  potential but also the particle radius are determining factors in stability properties has been suggested by a number of authors, but to the best of our knowledge, no satisfactory explanation has previously been given. Indeed, the comparative lack of systematic experiments on the rôle of particle size in coagulation is indicative of the failure to appreciate this property.

#### 4. Notation.

For the convenience of readers we define again the chief symbols introduced in this paper:

- $a$ , radius,
- $Q$ , charge,
- $\zeta$ , electrokinetic potential, } of a colloidal particle.
- $\gamma$ , concentration of electrolyte in mol./l.
- $\kappa$ , characteristic quantity in the Debye-Hückel theory of electrolytes  
 $= \sqrt{\gamma/3.04 \times 10^{-3}}$  at temperature  $T = 18^\circ \text{C}$ .
- $\tau = \kappa a$ .
- $R$ , distance between the particles.
- $s = R/a$ , distance between the particles in units of the radius.
- $D$ , dielectric constant of the solution.
- $kT_0 = 4 \times 10^{-14}$  ergs.
- $Y = Q/(180 kT_0 Da)^{\frac{1}{2}}$ ,
- $y = Q/(180 ADa)^{\frac{1}{2}} = Y(kT_0/A)^{\frac{1}{2}}$ , } measures of the charge.
- $A$ , constant in van der Waals energy between two particles.
- $E = F + V$ , total mutual energy between two particles = electrical energy + van der Waals energy.
- $E_{\text{con.}} = E_{\text{con.}} + V_{\text{con.}}$ ,  $R = 2a$ ,  $s = 2$ ,
- $E_{\text{con.}} = wkT_0$ ,  $F_{\text{con.}} = vkT_0$ , } at contact of two particles.
- $E_{\text{max.}} = F_{\text{max.}} + V_{\text{max.}}$ ,  $s_{\text{max.}} = s_m = R_{\text{max.}}/a$ , at maximum in the mutual energy.
- $U = E/A$ , a measure of the total mutual energy.
- $Z = 10^{-7} D \zeta^2 / A$ , a measure of the electrokinetic potential.

In conclusion we wish to express our appreciation to Profs. R. H. Fowler, E. K. Rideal and J. E. Lennard-Jones for their interest and help. In particular we are greatly indebted to Drs. F. Eirich, A. S. C. Lawrence and J. J. Bikerman for extremely helpful discussions on the experimental points. One of us (S. L.) is indebted to the Department of Scientific and Industrial Research for an assistantship to Prof. Lennard-Jones held during 1938-39. The other of us (G. P. D.) owes his thanks to the Managing Committee, Rajput College, Agra (India), for granting him leave of absence and also wishes to express his sincere thanks to Prof. Louis de Broglie for permitting him to stay at his institute.

### Summary.

A number of applications of the mutual energy between two colloidal particles is given. Our results suggest that there is no particular upper limit or range of values to the particle size in stable sols. An explanation is given of stepwise coagulation and peptisation, *i.e.* that stability of a sol decreases with increasing particle size. The new form for the rate of slow coagulation in which the interaction of the particles is introduced is indicated. A simple explanation is given of the fact that electrolytes which coagulate at high concentrations (*e.g.* alkali halides) also have high critical  $\zeta$  potentials. Finally the method of determining the critical  $\zeta$  potential or the potential at rapid coagulation as a function of the particle radius, electrolyte concentration and van der Waals' energy of attraction is illustrated and qualitative agreement with experiment is obtained.

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## THE SIGNIFICANCE OF THE PHENOMENON OF THE ELECTRICAL CHARGE ON THE STABILITY OF HYDROPHOBIC DISPERSIONS.

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### 1. Introduction.

Basing themselves on Donnan's<sup>1</sup> suggestion that the electrical double layer prevents the particles of a colloidal hydrophobic dispersion from coagulating, if their kinetic energy is insufficient to cause its total piercing on impact, Ellis<sup>2</sup> and Powis<sup>3</sup> carried out experiments to establish a relation between the drop in potential in the double layer of oil droplets in water to the stability of the dispersion. The latter made comparative stability- and cataphoretic measurements with emulsions to which KCl, BaCl<sub>2</sub>, AlCl<sub>3</sub> and ThCl<sub>4</sub> had been added, and concluded that on addition of each of these chlorides there is a narrow concentration range in which the stability decreases considerably, whereas the electrokinetic potential remains practically the same; this "critical potential" was alleged to have the same value, namely 30 mV., for the four salts examined. His observations are tabulated in columns 1, 2 and 3 of our Table IV, page 235, and represented in our Fig. 4, from which it will be seen that these figures are a very weak basis for the theory of the "critical potential," which is mainly founded on them.

In a subsequent publication, Powis<sup>4</sup> pointed out that an As<sub>2</sub>S<sub>3</sub> sol showed no constant critical potential for KCl, BaCl<sub>2</sub>, AlCl<sub>3</sub>, Th(NO<sub>3</sub>)<sub>2</sub> and HCl, but that at the flocculation value for KCl and for HCl, the electrokinetic potential was appreciably higher (44 and 50 mV.) than for the salts with polyvalent cations (about 26 mV.).

<sup>1</sup> F. G. Donnan, see Ellis, *Z. physik. Chemie*, 1912, 80, 597.

<sup>2</sup> R. Ellis, *ibid.*, 1912, 78, 321; 1912, 80, 597; 1915, 84, 145.

<sup>3</sup> F. Powis, *ibid.*, 1915, 89, 91, 179, 186.

<sup>4</sup> F. Powis, *J. Chem. Soc.*, 1916, 109, 734.



The extensive measurements made by Limburg<sup>5</sup> on emulsions of pure paraffin oil in water, clearly showed that the stability of such a colloidal system is not exclusively governed by the electrokinetic potential, but that also other factors play a part. Thus Limburg saw that by adding potassium carbonate to the emulsion the cataphoretic velocity increased, whereas the stability decreased. Besides the electrokinetic potential he considered the electric conductivity of the outer phase and the interfacial tension important for the stability of the system.

Kruyt, Roodvoets and v. d. Willigen<sup>6</sup> confirmed Powis' statement that near the flocculation value for different electrolytes, an  $As_2S_3$  sol does not show a constant electrokinetic potential when calculating in the usual way by substituting in the formula the values for the dielectric constant and the viscosity of the water phase. They point out that the discrepancy between the different "critical potentials" is perhaps due to the fact that the dielectric constant and the viscosity of the double layer should be used instead. These values not being known, the "theory of the critical potential" could not be checked.

In the following pages we shall try to establish an approximate relation between the electric boundary phenomena and the stability of the system, which tallies better with the experimental data than the hypotheses of a constant "critical potential."

## 2. The Relation between the Stability and the Electric Boundary Phenomena of Hydrophobic Colloids.

In Donnan's<sup>1</sup> working hypotheses, cited in the preceding section, the stability of the system is brought into relation with the opponent action of the kinetic energy of the particles, leading to collision and a magnitude, originating in the electric boundary phenomena, preventing it. This magnitude, since it can make equilibrium with the kinetic energy, must also be of the dimension of an energy, and will be equivalent to the energy needed to bring two particles originally at infinite distance, against the action of their electric field, to collision.

Briggs,<sup>7</sup> too, brought the energy of the electric repulsion to the fore, but took no account of the presence of ions in the field between the two particles, and simply applied Coulomb's law to globules with a surface-potential equivalent to the electrokinetic potential.

The presence of the mobile part of the double layer, however, limits the extension over which the electric forces act to a considerable extent. We did not succeed in making an exact calculation of the energy required to cause collision between two mutually approaching particles, against the action of the double layers. We have therefore tried to draw up the simplest possible empirical formula with the correct dimensions.

The dimension formula of energy can be written :  $(M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1})^2 \times (L)$ , *i.e.* the square of a potential multiplied by a length.

For this potential we took the electrokinetic potential, *i.e.* the energy required to transfer an electron from the outer phase to the plane where a shift takes place in case of electrophoresis ; for the magnitude with the dimension  $(L)$ , we naturally chose  $1/\kappa$ , the average thickness of the ion

<sup>5</sup> H. Limburg, *Rec. trav. chim. Pays Bas.*, 1926, 45, 772, 854, *Thesis*, Delft, 1924.

<sup>6</sup> H. A. Kruyt, A. C. W. Roodvoets and P. C. v. d. Willigen, *Coll. Symp. Mon.*, 1926, 4.

<sup>7</sup> D. R. Briggs, *J. Physic. Chem.*, 1930, 34, 1326.

sphere occurring in the Debye-Hückel equation. The magnitude representing the energy required to overcome the repulsion caused by the electric double layers would therefore be formulated as :

$$A = c\zeta^2/\kappa.$$

We shall now see in how far this equation is in agreement with the experimental data.

If the kinetic energy of the two particles is smaller than this energy ( $A$ ) of electric repulsion, no collision would occur; if it is greater, it might. As the kinetic energy of the individual particles may deviate rather much from the average kinetic energy there is a possibility that two particles with a greater energy than the average collide at a value of  $A$  greater than that of the average kinetic energy of the particles. Moreover, the probability of sticking, under a collision with only little remaining energy, may be smaller than under a much more vigorous collision. The sudden transition from a stable to an unstable system, anticipated on account of the foregoing, will therefore become a more gradual one.

The drop in  $\zeta$  value observed by Powis during the aging of emulsions to which electrolyte has been added, by which he accounts for the often sudden coagulation under storage, has, in the light of the views developed

above, of course the same influence on the stability of the system.

In experiments relative to the peptisation of a flocculated sol by washing out, Powis and other authors have observed, for instance, with the negative  $\text{As}_2\text{S}_3$  sol, that this is easy if the sol had been flocculated by the addition of large quantities of salt with a monovalent cation, but difficult if the flocculation took place by a small amount of salt with polyvalent cations. This, too, may be very well accounted for by the formula derived above: the first instability had been caused by a high  $\kappa$  value, which is at once reduced by washing out; the second by a low value for  $\zeta$ , which is caused by the negative colloidal particle having absorbed positive ions, which are much more difficult to remove.

In a  $\zeta - \sqrt{\Sigma(cz^2)}$  diagram the conditions with the same energy of electric repulse of the particles lay on a parabola passing through the origin, with the  $\sqrt{\Sigma(cz^2)}$  axis as axis of symmetry and  $A/4c$  as focal length ( $c$  = the concentration of the ion,  $z$  = the valency of this ion,  $c_2$  = constant factor).

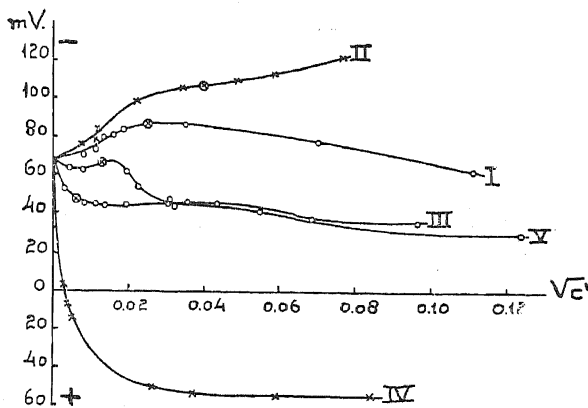


FIG. I.— $\zeta - \sqrt{\Sigma cz^2}$  curves for paraffin oil emulsions and electrolyte solutions, according to Limburg's experiments.

$\zeta$  Calculated in accordance with Henry.

- |                               |                        |
|-------------------------------|------------------------|
| I. KCl.                       | III. $\text{BaCl}_2$ . |
| II. $\text{K}_2\text{CO}_3$ . | IV. $\text{AlCl}_3$ .  |
|                               | V. HCl.                |

In such a diagram the successive stability levels of the dispersion are represented by a bundle of such parabola with focal lengths, proportional to the energies of electric repulse of the particles.

### 3. Relation between the Stability of Oil in Water Emulsions and the Energy of Electric Repulse of the Particles.

#### (a) Experiments by Limburg.<sup>5</sup>

From Limburg's principal data on the cataphoretic velocity of droplets of an emulsion of pure paraffin oil in water, the value of the  $\zeta$  potential was calculated with Henry's formula. The values obtained for  $\zeta$  and  $\zeta^2/\kappa$  (the  $\zeta$  value in millivolts was used for the calculation) are plotted against the square root of the salt concentration (Figs. I and II).\*

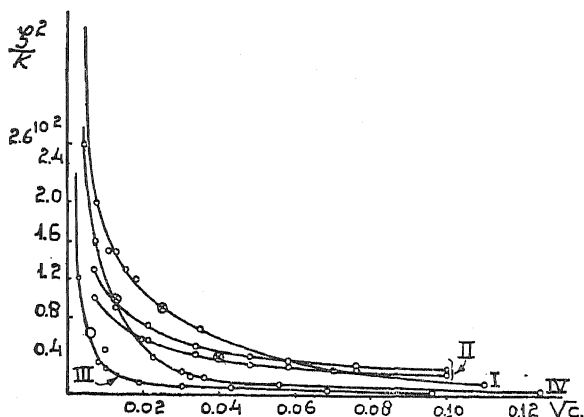


FIG. II.— $\zeta^2 - \sqrt{c}$  curves for paraffin oil emulsions in electrolyte solutions, according to Limburg's experiments.

I. KCl                      III. BaCl<sub>2</sub>.  
II. K<sub>2</sub>CO<sub>3</sub>.              IV. HCl.

deduced; they are tabulated in Table I and in graph III the stability is plotted against  $\zeta^2/\kappa$ . In graphs I and II the values of  $\zeta$  and  $\zeta^2/\kappa$  at which the stability of the emulsion after 24 hours' slow shaking is about 90 %, have been indicated by 0. These values have been collected in Table II.

Whereas the values of  $\zeta$  at which the instability of the emulsion is perceptible

are higher, lower or equal to that for the stable emulsion without the addition of any electrolyte, the values for  $\zeta^2/\kappa$  decrease gradually with the addition of electrolyte, and in all cases coagulation sets in when this value is lower than only 2 % of this magnitude for the emulsion without the addition of electrolyte.

As to the relatively small variations in the critical values of  $\zeta^2/\kappa$ , we would observe the following: Limburg's values for the stability of the emulsions to which BaCl<sub>2</sub> has been added are not quite comparable with the others. He states in his thesis that during this test the shaking apparatus had stopped for an unknown length of time. The stability in pure water found in this series, just as that in the series with stagnant KCl solutions, is appreciably lower than in the other series (93-94 % against 97-100 % in the other tests). If we take this into account, and make a comparison with the difference between the stability in moving

\* The calculation of the  $\zeta^2/\kappa$  values on addition of K<sub>2</sub>CO<sub>3</sub> was based on the assumption that this salt is dissociated in  $2K^+ + CO_3^{2-}$  as well as in  $2K^+ + H_2CO_3 + 2OH^-$ .

TABLE I.—THE STABILITY OF EMULSIONS OF PARAFFIN OIL IN WATER WITH ADDITION OF ELECTROLYTE, AND THE CORRESPONDING VALUES OF  $\zeta$  AND  $\zeta^2/\kappa$ ; DETERMINATIONS BY LIMBURG.

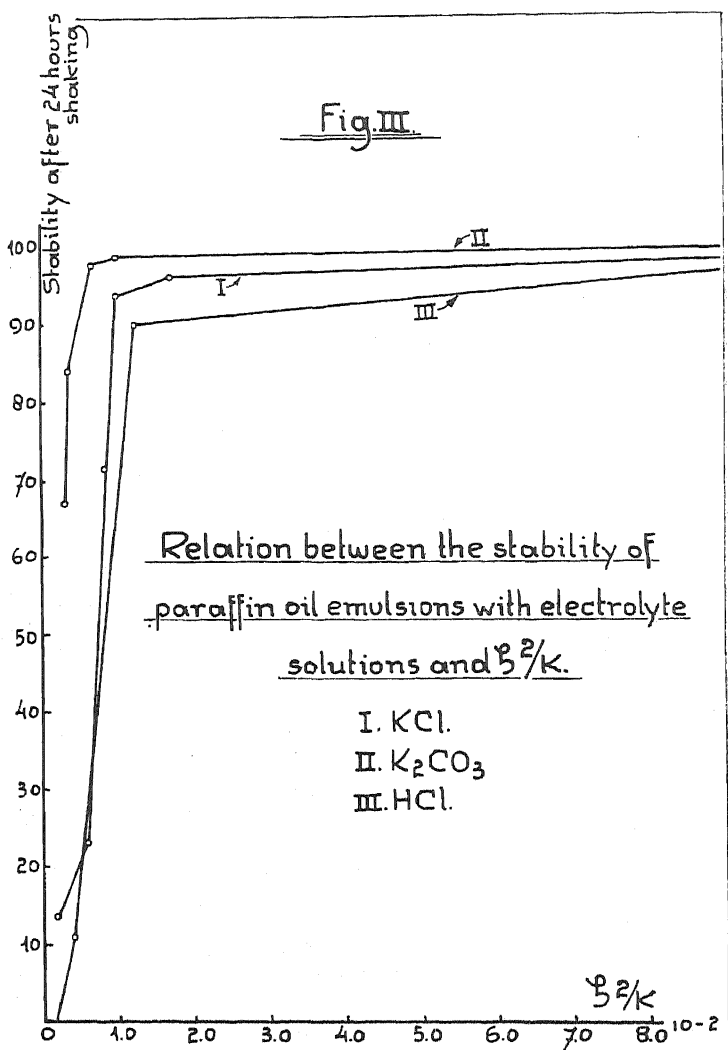
Concentration in mol./litre.	Stability of the Emulsion.	$\zeta$ (Millivolt).	$\zeta^2/\kappa$ .
<b>KCl series</b>			
Pure water	0.985	— 69	abt. $47 \cdot 10^{-2}$
$1.0 \cdot 10^{-4}$ KCl	0.966	— 74	$1.72 \cdot 10^{-2}$
$5.0 \cdot 10^{-4}$ „	0.937	— 86	$0.98 \cdot 10^{-2}$
$1.0 \cdot 10^{-3}$ „	0.721	— 88	$0.76 \cdot 10^{-2}$
$2.5 \cdot 10^{-3}$ „	0.234	— 84	$0.46 \cdot 10^{-2}$
$1.0 \cdot 10^{-2}$ „	0.138	— 68	$0.12 \cdot 10^{-2}$
<b>K<sub>2</sub>CO<sub>3</sub> series</b>			
Pure water	0.992	— 69	abt. $47 \cdot 10^{-2}$
$9.6 \cdot 10^{-5}$ K <sub>2</sub> CO <sub>3</sub>	0.989	— 80	$1.0 \cdot 10^{-2}$
$4.8 \cdot 10^{-4}$ „	0.982	— 99	$0.64 \cdot 10^{-2}$
$9.6 \cdot 10^{-4}$ „	0.969	— 105	$0.50 \cdot 10^{-2}$
$2.4 \cdot 10^{-3}$ „	0.843	— 110	$0.37 \cdot 10^{-2}$
$9.6 \cdot 10^{-3}$ „	0.670	abt. — 140	$0.30 \cdot 10^{-2}$
$2.4 \cdot 10^{-2}$ „	0.347	„ — 140	$0.10 \cdot 10^{-2}$
<b>HCl series</b>			
Pure water	0.971	— 69	abt. $47 \cdot 10^{-2}$
$1.2 \cdot 10^{-4}$ HCl	0.90	— 65	$1.2 \cdot 10^{-2}$
$6.2 \cdot 10^{-4}$ „	0.11	— 51	$0.34 \cdot 10^{-2}$
$1.2 \cdot 10^{-3}$ „	0.00	— 45	$0.17 \cdot 10^{-2}$
<b>BaCl<sub>2</sub> series *</b>			
Pure water	0.928	— 69	abt. $47 \cdot 10^{-2}$
$1.8 \cdot 10^{-4}$ BaCl <sub>2</sub>	0.821	— 45	$0.22 \cdot 10^{-2}$
$9.4 \cdot 10^{-4}$ „	0.587	— 46	$0.08 \cdot 10^{-2}$
$3.7 \cdot 10^{-3}$ „	0.491	— 42	$0.06 \cdot 10^{-2}$
<b>AlCl<sub>3</sub> series</b>			
Pure water	1.00	— 69	abt. $47 \cdot 10^{-2}$
$6.5 \cdot 10^{-7}$ AlCl <sub>3</sub>	0.83	—	—

\* In this experiment the stirring apparatus had stopped for an unknown length of time.

TABLE II.—VALUES OF  $\zeta$  AND  $\zeta^2/\kappa$  AND OF THE INTERFACIAL TENSION AT WHICH THE STABILITY OF THE EMULSION AFTER 24 HOURS' SHAKING IS ABOUT 90 PER CENT. (CALCULATED FROM LIMBURG'S EXPERIMENTS): FOR COMPARISON THE VALUES FOR THE STABLE SYSTEM IN PURE WATER.

Flocculating Reagent.	Concentration in mol./litre at which the Stability is 90 % or less.	Relative Interfacial Tension at this Salt Concentration.	$\zeta$ at which the Stability is 90 % or less.	$\zeta^2/\kappa$ at which the Stability is 90 % or less.
KCl	0.0005	0.99	— 86 or lower	$0.9 \cdot 10^{-2}$ or lower
HCl	0.00012	1.00	— 68 „ „	$1.0 \cdot 10^{-2}$ or lower
BaCl <sub>2</sub>	abt. 0.00004		abt. — 48	( $0.6 \cdot 10^{-2}$ or lower)
K <sub>2</sub> CO <sub>3</sub>	abt. 0.0015	0.82	— 107 or higher	abt. $0.4 \cdot 10^{-2}$ or lower
in pure water		1.00	— 70	abt. $47 \cdot 10^{-2}$

and stagnant liquids when KCl is added, it becomes likely that in strictly comparative tests a somewhat higher value for  $\zeta^2/\kappa$  will be found at the initial coagulation by  $\text{BaCl}_2$  than those now calculated, and that this will be nearer the critical value for KCl and HCl.



The experiments on the influence of  $\text{AlCl}_3$  on the stability and charge of the emulsion are of no use for our purpose, as in the area of initial instability (about  $0.000006 \text{ N. AlCl}_3$ ) no cataphoresis experiments have been made.

The comparatively low value for  $\zeta^2/\kappa$  at initial instability when  $\text{K}_2\text{CO}_3$  is added is probably due to the increased stability by a decrease in interfacial tension. This influence also makes itself clearly felt when the tests in which 0.5 % of oleic acid had been added to the paraffin oil are compared with those with pure oil. The values at which then after 24 hours' shaking 90 % remained emulsified are tabulated in Table III.

TABLE III.—VALUES OF  $\zeta$  AND  $\zeta^2/\kappa$  OF EMULSIONS CONTAINING 0.5 PER CENT. OF OLEIC ACID ON PARAFFIN OIL, WHOSE STABILITY AFTER 22 HOURS' SHAKING IS ABOUT 90 PER CENT. (CALCULATED FROM LIMBURG'S EXPERIMENTS).

Flocculating Reagent.	Concentration in mol./litre at which the Stability is 90 % or less.	Relative Interfacial Tension at this Salt Concentration.	$\zeta$ at which the Stability is 90 % or less.	$\zeta^2/\kappa$ at which the Stability is 90 % or less.
KCl	0.001	0.68	— 87	$0.76 \cdot 10^{-2}$
HCl	0.00024	0.68	— 68	$0.80 \cdot 10^{-2}$
K <sub>2</sub> CO <sub>3</sub>	0.012	too small to be determined	— 124	$0.31 \cdot 10^{-2}$

TABLE IV.—THE STABILITY AFTER  $2 \times 24$  HOURS, THE  $\zeta$  POTENTIAL (CALCULATED WITH VON SMOLUCHOWSKI'S EQUATION), AND THE VALUE OF  $\zeta^2/\kappa$  IN POWIS' MOST IMPORTANT EXPERIMENTS WITH EMULSIONS OF CYLINDER OIL IN ELECTROLYTE SOLUTIONS.

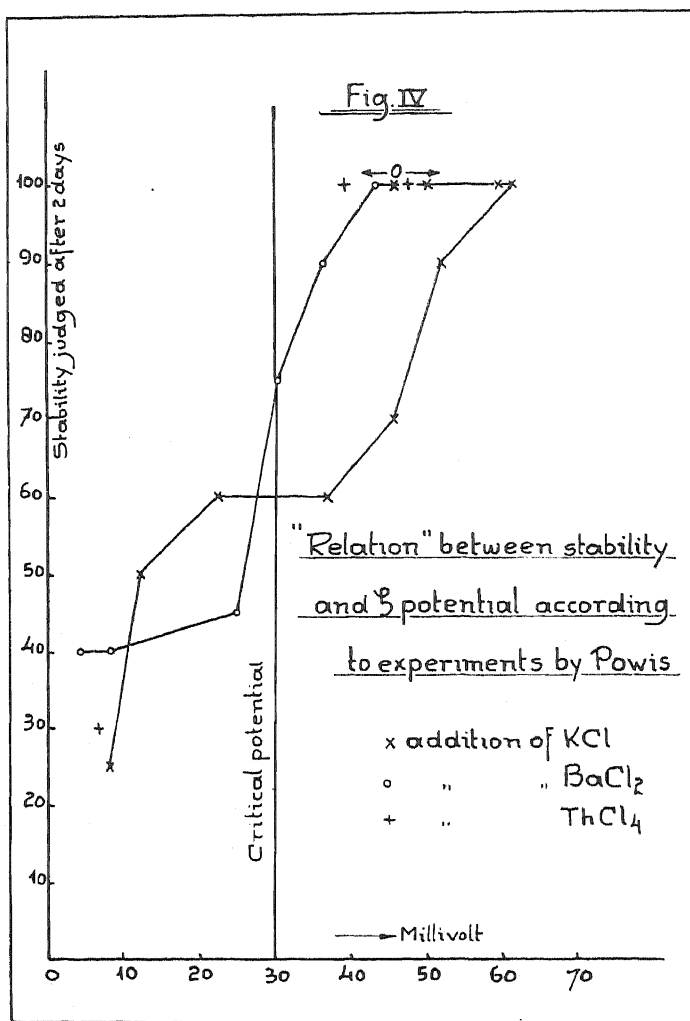
Concentration of the Salt in mol./litre.	Stability of the Emulsion.	$\zeta$ in Millivolts.	$\zeta^2/\kappa$ (for $\zeta$ in Millivolts).
Pure water	1.0	— 46	$20 \cdot 10^{-2}$
0.2 . $10^{-3}$ KCl	100	— 50.5	$0.55 \cdot 10^{-2}$
1 . $10^{-3}$ „	100	— 59.5	$0.34 \cdot 10^{-2}$
2.5 . $10^{-3}$ „	100	— 61.5	$0.23 \cdot 10^{-2}$
5 . $10^{-3}$ „	90	— 52	$0.11 \cdot 10^{-2}$
25 . $10^{-3}$ „	60	— 37	$0.03 \cdot 10^{-2}$
100 . $10^{-3}$ „	60	— 22	$0.005 \cdot 10^{-2}$
250 . $10^{-3}$ „	50	— 12	$0.0009 \cdot 10^{-2}$
500 . $10^{-3}$ „	20	— 8	$0.0003 \cdot 10^{-2}$
0.2 . $10^{-3}$ BaCl <sub>2</sub>	100	— 43.5	$0.23 \cdot 10^{-2}$
1 . $10^{-3}$ „	75	— 30.5	$0.05 \cdot 10^{-2}$
5 . $10^{-3}$ „	45	— 25	$0.02 \cdot 10^{-2}$
25 . $10^{-3}$ „	40	— 8	$0.0009 \cdot 10^{-2}$
0.005 . $10^{-3}$ AlCl <sub>3</sub>	100	— 42	$0.98 \cdot 10^{-2}$
0.01 . $10^{-3}$ „	75	— 38	$0.41 \cdot 10^{-2}$
0.05 . $10^{-3}$ „	5	— 17	$0.05 \cdot 10^{-2}$
0.2 . $10^{-3}$ „	15	— 8.5	$0.006 \cdot 10^{-2}$
0.001 . $10^{-3}$ ThCl <sub>4</sub>	100	— 47.5	$2.3 \cdot 10^{-2}$
0.005 . $10^{-3}$ „	100	— 39.5	$0.67 \cdot 10^{-2}$
0.01 . $10^{-3}$ „	30	— 6.5	$0.06 \cdot 10^{-2}$

Resuming, we can say that the assumption that the value of  $\zeta^2/\kappa$  governs the stability of the system fits in very well with Limburg's experiments, and that the rather small deviations can be easily explained.

#### (b) Experiments by Powis.

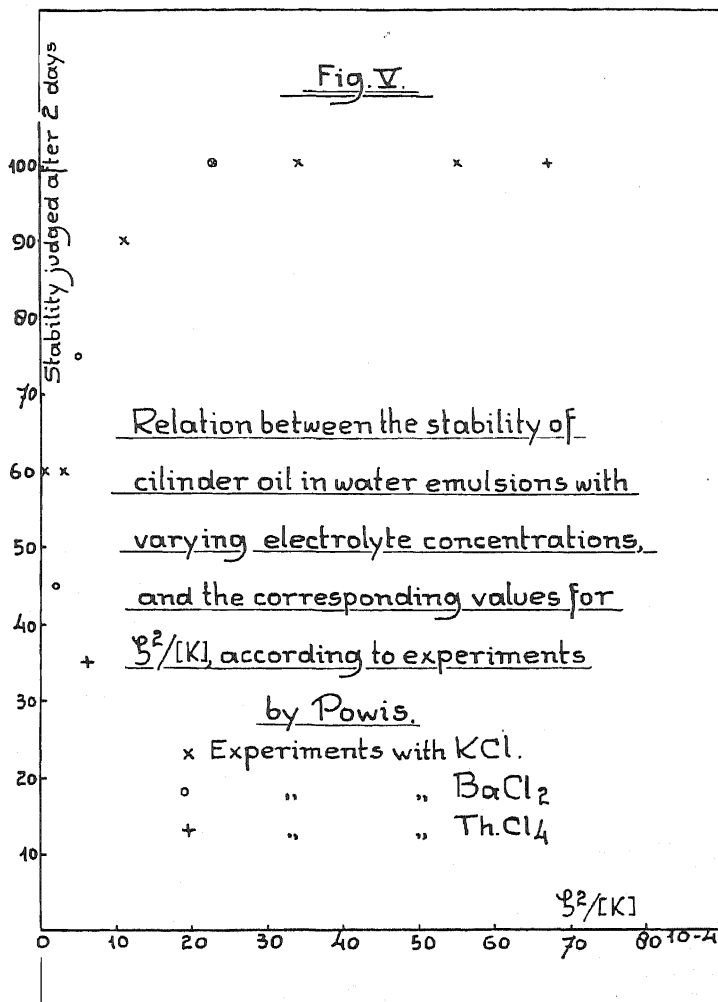
We shall now ascertain in how far the experiments with emulsions of Powis,<sup>3</sup> which formed the basis for the theory of the critical potential, may support the hypothesis that the value of  $\zeta^2/\kappa$  is the descriptive magnitude for the stability of the system. The principal experimental data have been collected in Table IV, in which the value for  $\zeta^2/\kappa$  has been calculated as well.

In this table we maintained the values stated by Powis which had been calculated with von Smoluchowski's formula from the cataphoretic velocity, as these values practically do not deviate from those found according to Henry's more exact formula. Only the determination in pure water would, calculated in accordance with Henry, give an appreciably higher value for  $\zeta$ , namely 69 mV.



The values of  $\zeta$  at which the coagulation sets in are, just as in Limburg's observations, higher in the case of KCl and lower in the case of salts with polyvalent cations than the value of this magnitude for the stable emulsion in water. The values for  $\zeta^2/\kappa$  vary in the measuring range between  $2 \cdot 10^{-1}$  and  $3 \cdot 10^{-6}$ . Instability occurs when this energy is less than 1 to 2 % of the original value. The series of experiments with KCl and BaCl<sub>2</sub> give exactly the same line for the relation between the magnitude examined and the stability (compare graphs IV and V),

while the few values determined for  $\text{ThCl}_4$  show greatly similar results. The series of experiments with  $\text{AlCl}_3$  seems to give a slightly higher value for the energy at which flocculation begins than the other series; it should, however, be taken into account that both  $\text{AlCl}_3$  and  $\text{ThCl}_4$  in these extreme dilutions may cause complications by hydrolytic dissociation. Powis therefore used a concentrated stock solution and determined the cataphoretic velocity at once after diluting and mixing



with the emulsion. The stability value on the contrary refers to emulsions which have been standing for 2 days and in which this dissociation may have caused the formation of much more easily adsorbed colloidal metal oxide, thus lowering the value of  $\zeta$  on standing.

The few values which can be calculated from Ellis' experiments also give a highly satisfactory relation between the stability of emulsions and the value of  $\zeta^2/\kappa$ .



The data available in colloid chemical literature on the stability of emulsions of pure oil in electrolyte solutions therefore largely confirm the conception that the magnitude  $\zeta^2/\kappa$  determines the stability of such a system as far as this depends on boundary electric phenomena.

#### 4. Application of the Function $\zeta^2/\kappa$ for Judging the Stability of Suspensoids.

The colloid chemical literature contains only few data on hydrophobic dispersions which are suitable to test hypotheses on a quantitative relation between stability,  $\zeta$  potential and electrolyte concentration.

In some cases in which the publication gives a sufficient amount of figures, a closer consideration shows these to be unsuitable to be incorporated in the above formula, as the examined sol is contaminated with electrolytes formed by the chemical reaction. We shall give an example in which the concentration of *contaminating electrolytes* could be calculated, which is rarely the case.

Briggs<sup>7</sup> examined the relation between cataphoretic velocity and flocculation of a *gold sol* obtained from  $\frac{1}{4}$  millimol of  $\text{NaAuCl}_4$  per litre by means of  $\text{H}_2\text{O}_2$  and 1.5 millimol of  $\text{NaOH}$ . This gold sol therefore contains 1.75 millimol of 1-1 valent electrolyte ( $\text{NaOH} + \text{NaCl}$ ). In Table V we have tabulated the flocculation value, with the appertaining values for cataphoretic velocity  $U$  and the magnitude  $\frac{U^2}{\sqrt{\Sigma(cz^2)}}$ , which is practically proportional to  $\zeta^2/\kappa$ . The latter value is given in the assumption that the water phase exclusively contained the flocculating ions stated, as well as corrected for the 1.75 millimol of 1-1 electrolyte.

TABLE V.—INFLUENCE OF THE ELECTROLYTES WHICH CONTAMINATE A SOL ON THE VALUE OF  $U^2/\sqrt{\Sigma(cz^2)}$ , DEMONSTRATED BY BRIGGS' EXPERIMENTS WITH A GOLD SOL.

Flocculating Electrolyte.	Flocculation Value in mol./litre.	At the Flocculation Value		
		Cataphoretic Velocity, $U$ .	$U^2/\sqrt{\Sigma(cz^2)}$ when the flocculating agent only was present.	$U^2/\sqrt{\Sigma(cz^2)}$ when corrected for the 1.75 mol. of 1-1 valent Electrolyte.
KCl . . . . .	24.0 . $10^{-3}$	3.65	6 . $10^1$	6 . $10^1$
Strychnin-nitrate . .	0.41 . $10^{-3}$	2.15	16 . $10^1$	7 . $10^1$
$\text{BaCl}_2$ . . . . .	0.47 . $10^{-3}$	2.15	9 . $10^1$	6 . $10^1$
$\text{AlCl}_3$ . . . . .	0.0043 . $10^{-3}$	2.15	64 . $10^1$	8 . $10^1$
For the stable sol without any addition the values were . . . . .		3.9		26 . $10^1$

This table shows that whereas the critical value of the electric repulse calculated only from the concentrations of the added electrolyte has a variation of 1 to 10; the variation of this energy is only 1 : 1.3 after correction for the contaminations of the sol. The critical value of the energy of electric repulse is about  $\frac{1}{4}$  of the value for this magnitude for the original sol.

It is also apparent from this table why in different investigations the existence of a critical potential was seemingly confirmed with deviating concentration of the flocculating reagent added: the systems examined contained so much electrolyte as contamination that variations in  $\sqrt{\Sigma(cs^2)}$  caused by the addition of the flocculating electrolyte are very small in comparison to the changes in stability caused by the variation in  $\zeta^2$ .

For most of the sols described in the literature it is difficult to calculate the contaminations, as the electrolyte formed during the manufacture is, at least in part, removed by washing out, dialysis, etc. Although the error by neglecting this electrolyte concentration will not be so great in these cases as with the gold sol described, this incalculable factor will yet have to be reckoned with.

The most suitable experiments for recalculation are those made with  $As_2S_3$  sol by various authors. In these experiments the flocculation value of an electrolyte, that is, that concentration of the electrolyte which after a previously fixed time causes a previously fixed degree of flocculation, was related to the electrokinetic potential when the quantity of electrolyte was added. In most of the experiments, however, the time fixed for the determination of the flocculation value was so short that it was impossible to determine the cataphoretic velocity under these conditions, and the electrokinetic potential had to be determined by extrapolation, making the result less accurate.

The flocculation value is found by interpolation between concentrations of the electrolyte at which flocculation occurs and those at which it does not. The limits between which the flocculation value is said to lie are rather wide in some publications to be discussed so that also the value of  $\kappa$  at the flocculation value is rather uncertain.

From the above it follows that we cannot expect a very constant value for the critical energy of repulse by the various salts used in these investigations. Still the results tally well with our formula. We mention the experiment of Powis<sup>4</sup>, which showed him already the inconsistency of the critical potential. Table VI gives the values relating to these experiments.

TABLE VI.—THE VALUES OF  $\zeta^2/\kappa$  AT THE FLOCCULATION VALUE OF  $As_2S_3$  SOL WITH DIFFERENT ELECTROLYTES, CALCULATED FROM THE FIRST DETERMINATION OF POWIS.

Electrolyte.	Concentration at the Flocculation Value in Millimol per Litre.	Potential in Millivolt at Flocculation Value.	$\zeta^2/\kappa$ .
KCl . . . .	40 . $10^{-3}$	— 50	3.8 . $10^{-4}$
HCl . . . .	30 . $10^{-3}$	— 50	4.4 . $10^{-4}$
BaCl <sub>2</sub> . . . .	0.5 . $10^{-3}$	— 25	4.9 . $10^{-4}$
AlCl <sub>3</sub> . . . .	0.05 . $10^{-3}$	— 21	7.7 . $10^{-4}$
Th(NO <sub>3</sub> ) <sub>4</sub> . . . .	between 0.05 . $10^{-3}$ and 0.10 . $10^{-3}$	— 27 to — 24	10 . $10^{-4}$ to 5.6 . $10^{-4}$

The values of  $\zeta^2/\kappa$  are, in view of the great inaccuracy (possible deviation in the determination of  $\zeta$ , 20%, hence for  $\zeta^2/\kappa$  40%), in fairly good agreement.

Finally, we mention the investigation by Freundlich and Zeh<sup>8</sup> into the stability of arsenic trisulphide sol towards complex cobalt salts. These salts, with polyvalent cation, have the advantage over the more usual aluminium and thorium salts in that they do not form colloidal systems by hydrolytic dissociation. In this investigation the researchers based themselves on the supposition that the influence of the electrolyte addition on the electrokinetic potential can entirely be accounted for by Freundlich's adsorption isotherm; they sought a relation between the potential drop derived from the adsorption isotherm and the flocculation value of the sol. In the series of experiments with monovalent and with bivalent complex cobalt salts they saw, however, after an initial drop in  $\zeta$  potential in the cataphoresis experiments that this potential rose when more of this salt was added. As this was considered irreconcilable with the adsorption theory, it was ascribed to experimental errors and the cataphoresis experiments with these salts were stopped. Extrapolation, ignoring this rise, led to the assumption of a critical potential of about  $-26$  mV. The only  $\zeta$  potential determined in the region of the flocculation value is, however,  $-45$  mV. We can now calculate from the flocculation values for the various complex cobalt salts the appurtenant  $\zeta$  potential, as

$$\frac{\zeta_1^2}{\kappa_1} = \frac{\zeta_2^2}{\kappa_2}.$$

In Table VII the values thus calculated have been listed and, for comparison, the  $\zeta$  potentials determined by the authors at the closest possible lower electrolyte concentration, stating the direction of the slope of the  $\zeta$ -concentration curve over the last range measured. The value of  $\zeta$  at the flocculation point will therefore probably be higher or lower than the last value stated according as the slope rises or drops in the last range measured.

TABLE VII.—CALCULATION OF THE  $\zeta$  POTENTIAL OF  $As_2S_3$  SOLS AT THE FLOCCULATION POINT WITH COMPLEX COBALT SALTS FROM FREUNDLICH AND ZEH'S EXPERIMENTS. FOR COMPARISON, THE NEAREST  $\zeta$  VALUES DETERMINED.

Electrolyte.	Flocculation Value (after Deducting the Amounts Absorbed to the Sol.).	$\zeta$ Potential at the Flocculation Value in — mV.	Last $\zeta$ Potential Measured.	Direction of Slope.
$[Co(NH_3)_4(NO_2)_2]Cl$	1255	87	82	rising
$[Co(NH_3)_5Cl]Cl_2$	101	61	54	"
$[Co(NH_3)_6]Cl_3$	14.3	45	45	base of calc.
$[(NH_3)_4Co \begin{array}{c} \nearrow NH_2 \\ \searrow OH \end{array} Co(NH_3)_4] Cl_4 \cdot 4H_2O$	2.9	34	41	falling
$[Co \begin{array}{c} \nearrow OH \\ \searrow OH \end{array} Co(NH_3)_4]_3 Cl_8$	2.3	38	39.5	falling

Table VII shows that in these experiments the values for the  $\zeta$  potential at the flocculation value, calculated with the formula for the critical value of the electric energy, are very close to the observations of the

<sup>8</sup> H. Freundlich and H. P. Zeh, *Z. physik. Chemie*, 1924, 114, 65.

$\zeta$  potential at the highest electrolyte concentration under the flocculation point and that a critical potential of  $-26$  mV, as assumed by the authors on the strength of these data, is improbable.

### Summary.

The data on which the relation between the  $\zeta$  potential and the stability of the lyophobic colloidal systems, described in colloid chemical literature, are based, are criticised. It is demonstrated that the assumption of a "critical potential" has no adequate foundation, but that the factor which predominates the stability of such a system, is the energy required to bring together two particles of the dispersion against the action of their electric field.

The following formula may be derived for this energy :

$$A = C_2 \frac{\zeta^2}{\kappa},$$

where  $\zeta$  = the electrokinetic potential and  $\kappa = 10^{7.364} \sqrt{\Sigma(cz^2)}$ .

According to this hypothesis the stability of the system is therefore determined by the electrokinetic potential and by the concentration and valency of the ions present in the water phase. This formula is applied to the data on the stability of oil in water emulsions collected by Limburg and Powis, and the results tally satisfactorily with their experiments. The formula is then also applied to suspensoids, *i.e.*,  $As_2S_3$  sol. It is found to account better, at least qualitatively, for the experiments than the assumption of a critical potential.

The often neglected influence on the sol is pointed out of rather small quantities of electrolytes which will not diminish the  $\zeta$  potential, but which greatly influence the value of  $\kappa$ .

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## THE ELECTRICAL DOUBLE LAYER IN RELATION TO THE STABILISATION OF EMULSIONS WITH ELECTROLYTES.

By D. F. CHEESMAN AND A. KING.

*Received 24th June, 1939.*

The most plausible of the theories of emulsion stabilisation is that which conceives an emulsion to be a type of colloidal suspension. The interface between two liquids, just as that between a solid and a liquid, may become the seat of an electrical double layer, which serves for the stabilisation of a dispersion of one phase in the other.

Stabilised emulsions are, in general, systems of three phases and three components. The third phase consists of an interfacially adsorbed film of the so-called "emulsifying agent," which is commonly considered to retain its phase identity within the emulsion. The term "emulsifying agent" embraces a wide variety of substances, such as the soaps, finely divided solids, and protective colloids, such as gelatin, agar-agar, and the natural gums. These substances have but one feature in common: they are surface-active. The interfacial film

which they form enriches the concentration of positive ions in the aqueous phase, by a process whose nature varies with the system concerned. The layer of negative ions which remains associated with the film, together with the positive counter-ions in the water, form the electrical double layer.

The double layer is not, however, held solely responsible for emulsion stability. The agent also exerts stabilising power by :

(a) The reduction of the interfacial tension between the phases. The less is the interfacial energy, the less will be the tendency for a reduction of the interfacial area by a coalescence of the globules.

(b) The purely mechanical effect of a rigid interfacial film. This may well be the source of a large measure of the stability of emulsions made with protective colloids.

Stable emulsions which do not incorporate an emulsifying agent are confined, in the general conception, to dilute oil hydrosols. These are very dilute dispersions of oils in water, which apparently owe their stability to the electrical double layer, coupled with the mutual remoteness of the globules.

In this laboratory we have recently discovered instances in which the electrical double layer is itself capable of imparting stability to concentrated emulsions, without the aid of surface active materials. Such a phenomenon lends support to the hypothesis of the double layer, and provides a means whereby the electrical effects in emulsions may be investigated in a more comprehensive manner than has hitherto been possible.

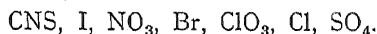
The observations to which we refer have already been recorded in the literature.<sup>1</sup> We have since engaged ourselves in a systematic research which now enables us to put forward generalisations. The qualitative results of our work may be set out as follows :

(a) Certain electrolytes are capable of stabilising emulsions of water in polar organic liquids, or of polar organic liquids in water.

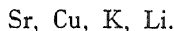
(b) The stabilising effect of the electrolytes is evident over a limited concentration range.

(c) The stabilities of the emulsions are dependent upon the electrolyte concentrations. A well-defined optimum concentration exists in every case.

(d) If the ions of potassium salts are arranged in the order of the decreasing stabilities which they are capable of imparting to an emulsion of water in amyl alcohol, we have :



(e) If the cations of divers chlorides be arranged in similar order, we have :



(f) The globules of the water in oil emulsions stabilised with electrolytes are positively charged, while those of the opposite type are negatively charged.

## Experimental.

### (1) Preliminary Experiments.

Experiments of a qualitative nature were carried out in order to ascertain which electrolytes possessed emulsifying properties in respect

<sup>1</sup> D. F. Cheesman and A. King, *Nature*, 1938, 141, 1099.

of the system amyl alcohol/water. The results are set out in Table I. The letter M after the name of an electrolyte signifies that the optimum concentration of this substance gives an unstable, but definite, emulsion.

TABLE I.

<i>Emulsion.</i>	<i>No emulsion.</i>
Potassium chloride	Potassium sulphate
Potassium dichromate	Potassium chromate
Potassium iodide	Potassium ferrocyanide
Potassium nitrate	Potassium persulphate
Potassium bromide	Potassium ferricyanide
Potassium chlorate	Sodium thiosulphate
Potassium carbonate (M.)	Sodium phosphate
Sodium sulphide	Magnesium sulphate
Aluminium nitrate	Lithium chloride
Cupric nitrate	Thorium sulphate
Cupric chloride	Ferrous sulphate
Potassium permanganate	Sodium baborate
Sodium hydroxide	Sodium bicarbonate
Ammonium chloride	
Sodium oleate	
Sodium benzene disulphonate (M.)	
Stannous ammonium chloride (M.)	
Ammonium iodide	
Ammonium thiocyanate	

## (2) Accurate Stability Measurements.

The system amyl alcohol/water was chosen for our quantitative investigations. Water in oil emulsions were prepared with a variety of salts, and the emulsion stability/electrolyte concentration relationships were studied.

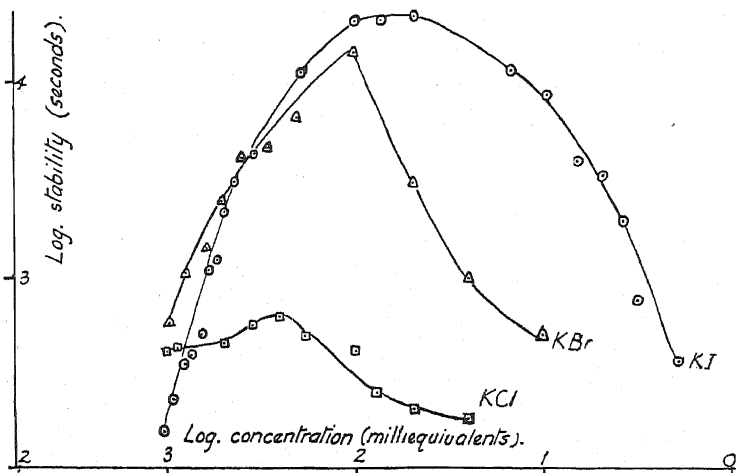


FIG. 1.

The emulsions were prepared with equal initial volumes of both phases, in pyrex bottles, and in the absence of air. The latter precautions were taken in order that the pronounced effects of dissolved air, and of alkali from the glass, might be largely eliminated. The stabilities were measured in standard eudiometer tubes, the temperature of which was thermostatically controlled. The measure of stability was taken as the

time required for the meniscus between the separated internal phase and the unbroken emulsion to pass from the 5 c.c. to the 15 c.c. graduation of the eudiometer tube.

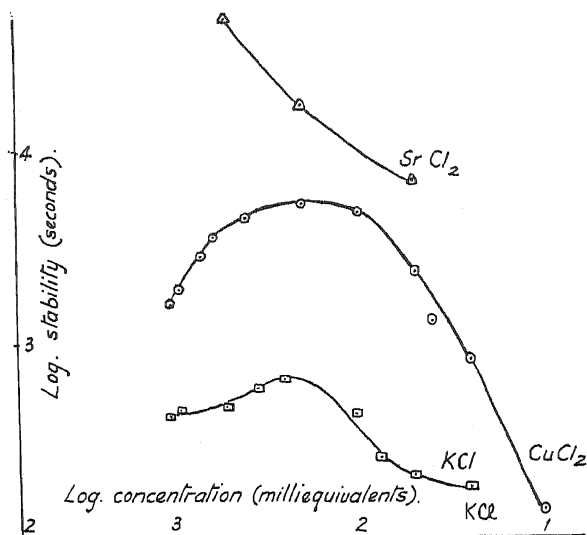


FIG. 2.

In Fig. 1 are shown the emulsion stability/electrolyte concentration curves for emulsions stabilised with the iodide, the bromide, and the chloride of potassium. In Fig. 2 the corresponding curves for the chlorides of strontium, copper, and potassium are drawn. The data are represented upon a logarithmic scale.

### (3) Interfacial Tension and Globule Charge.

The interfacial tensions between the phases in the series of systems containing potassium iodide were measured by the capillary method of Bartell and Miller.<sup>2</sup> No variations from the value for the system containing no electrolyte, beyond those accountable through experimental error, were observed.

The charge on the globules in the water in oil emulsions was found, by a simple cataphoretic method, to be positive in sign.

### Discussion.

From the curves in Fig. 1, and from the information given in the introduction, it will be seen that the stabilising powers of the anions are in the order of their positions in the lyotropic series. One cannot here enter into a general discussion of lyotropic phenomena. It may be noted, however, that the lyotropic series of the ions may be taken to represent the decreasing order of the hydrophobic tendency shown by those ions. Thus, the thiocyanate ion, which possesses little coagulative power with respect to colloidal suspensions, is thought to be far more hydrophobic than the sulphate ion, whose potency is great.

Assuming for a moment the truth of this hypothesis, let us consider its bearing on the subject of the present paper. The phenomenon now appears as follows:

Emulsions of water and organic polar liquids, in both types, are stabilised by the addition of electrolytes to the aqueous phase. The electrolytes are effective over only limited ranges of concentration, and only when the hydrophobic tendency of the anion is considerable.

<sup>2</sup> Bartell and Miller, *J. Amer. Chem. Soc.*, 1928, **50**, 1961.

The possession of a resultant positive charge by the globules brings some difficulty into the formulation of a theory. The empirical law of Coehn<sup>3</sup> might have been of assistance. He held that when two liquid phases were in contact, that with the lower dielectric constant must be negatively charged with respect to the other. The rule, however, is without theoretical foundation, and even without complete practical justification. It becomes necessary to resort to an ionic hypothesis. The polar non-aqueous phase would normally be considered as devoid of ions, save for the results of the dissociation of the minute amount of electrolyte dissolved therein. The ions for an electrical double layer, which must doubtless stabilise the water in oil emulsions, originate within the globules.

On the lyotropic hypothesis, we see that the most hydrophobic anions show the greatest power of emulsion stabilisation. Those salts with anions at the hydrophobic end of the lyotropic series are appreciably soluble in amyl alcohol. At the interface between amyl alcohol and water there will be a tendency for such ions to collect on the amyl alcohol side of the interface, while the more hydrophilic cations will collect in the aqueous phase. This means that a globule will bear at its surface the positive side of an electrical double layer, which will tend to the stabilisation of the emulsion.

There remains to discuss the reasons for the changes in emulsion stability which follow upon variations in the electrolyte concentration. To this end, let us employ Gouy's conception of the diffuse ionic layer. Gouy imagined a plate, which, when placed in an electrolytic solution, assumed a charge and a definite potential relative to the liquid. Assuming the complete dissociation of the electrolyte, and considering the distribution of the positive and negative ions in the solution near the plate, he arrived at the expression :

$$a = \sqrt{\frac{DRT}{4\pi N^2 \epsilon^2 (n_a + n_c) N_c n_c \text{ (or } N_a n_a)}}$$

where  $a$  is the distance of the plate from the centre of gravity of the ionic atmosphere,  $\epsilon$  is the charge on the ion,  $n_a$  and  $n_c$  are the valencies of the anion and of the cation,  $N_a$  and  $N_c$  are the numbers of gram ions in unit volume of the solution, and  $D$  is the dielectric constant of the solvent.

Now  $a$  may be taken as a measure of the effective thickness of the outer ionic layer. From the equation it follows that this thickness increases as (a) the dielectric constant of the solvent and the absolute temperature increase, and as (b) the ionic valencies and the ionic concentrations decrease.

An enlarged sphere of potency of the diffuse layer will tend to decrease the possibility of collision of two globules, and hence increase the stability of an emulsion. Here, then, is an explanation for the increase of the stabilities of our emulsions with decreasing electrolyte concentrations, in the section of the stability curve which extends from high concentrations to the optimum. It remains to consider the reasons for the falling off in stability when the concentration sinks below the optimum value, and for the differences in that value for different electrolytes.

<sup>3</sup> Coehn, *Wied. Ann.*, 1898, 64, 227.



At very low concentrations of electrolyte, the number of ions which cross from one phase to the other will be comparatively small, and the resultant effective charge on the globules will be insufficient to impart great stability to the emulsions. As the electrolyte concentration increases, the charge on the globule will be augmented. Simultaneously, in accordance with the law of Gouy, the effective thickness of the diffuse layer will decrease. There will thus come a time when the combined stabilising effects of the thickness of the diffuse layer and of the charge on the globule, will attain their resultant maximum. At this concentration, the emulsion formed from the two phases will exhibit its maximum stability.

By a continuation of such reasoning, there is no difficulty in explaining the shifting of the maximum in the stability/concentration curve which attends the changing of the anion. The more hydrophobic are the anions, the greater will be their migration into the oil phase, all other things being equal. As the charge on the globule depends upon the excess concentration of anions in the oil phase, the more hydrophobic anions will develop the most favourable relationship between the globule charge and the effective thickness of the double layer at lower electrolyte concentrations in the internal phase. The greater is the hydrophobic tendency of the anion, the less is the concentration of electrolyte for optimum emulsion stability. An examination of the stability curves will show that this is in concord with the experimental data.

In the interests of simplicity, the rôle of the cation has not yet been considered. The nature of that ion has been shown (Fig. 2) to influence greatly the properties of the emulsions. The stabilising effect of the increased valency is at once apparent. Various cations of the same valency have, however, different effects on the stabilisation of emulsions. Thus, the optimum stability obtainable with sodium iodide is considerably greater than that in the corresponding case with potassium iodide. It is generally held that the sodium ion is more hydrophilic than the potassium ion. With relation to the mechanism proposed above, this means that for corresponding concentrations of these electrolytes, the cationic impoverishment in the non-aqueous phase will be greater in the case of the sodium salt.

### Water Oleosols.

Certain systems have been discovered in which ions are provided for the stabilisation of emulsions of both types, without the aid of introduced electrolytes or surface active materials. Cyclic ketones, such as cyclohexanone and acetophenone, together with water, exhibit such behaviour. The water in oil emulsions are of special interest, in view of the fact that Clayton<sup>4</sup> questions the existence of such systems formed from pure components.

A water oleosol of water in pure cyclohexanone was subjected to a cataphoresis experiment. A definite migration of globules towards the cathode was noted. The only source of the positive charge lies in the migration across the interface of the ionisation products of one of the components, in accordance with the theory which has been expounded in the foregoing pages.

<sup>4</sup> Clayton, *Theory of Emulsions*, London, 1935, p. 2.

The composition of cyclohexanone and acetophenone, the only substances which have so far been observed to possess these remarkable properties, would suggest that the ketone group itself provided a hydrogen ion after undergoing keto-enol transformation. The investigation of such systems will provide an intriguing theme for further research.

The authors thank Dr. E. A. Guggenheim for his help in formulating the theory of the electrolyte stabilisation of emulsions.

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## PART III.—BIOLOGICAL AND TECHNICAL APPLICATIONS.

### THE USE OF ELECTROPHORESIS IN THE ELUCIDATION OF BIOLOGICAL PROBLEMS.

BY LAURENCE S. MOYER.

*Received 13th June, 1939.*

Electrophoresis is one of the most powerful tools at the disposal of the biologist for the investigation of the surface phenomena which are so intimately linked to biological processes. With this sensitive technique he is able to follow changes at the surface which are so minute as to render them virtually undetectable by other methods. For measurements of adsorbed films or living cells the microscopic method is most suitable. With it rapid changes at the surface of a single particle or cell can be followed with ease. Of the microelectrophoresis instruments available the one-piece flat glass cells with non-polarisable electrodes described by Abramson<sup>1</sup> and by Abramson, Moyer and Voet<sup>2</sup> have been shown to yield results, where comparisons are feasible, which agree with data obtained by other methods.<sup>3, 4</sup> In addition, the microscopic technique is not restricted to any particular range of ionic strength. The operation of these instruments and the precautions necessary to secure quantitative results have already been discussed in detail.<sup>5</sup> In this communication I shall present some recent investigations which exemplify this mode of approach.

#### The Relationship of Bacterial Surfaces to the Age of the Culture.

Numerous investigators<sup>6</sup> have demonstrated that bacteria from freshly made cultures are killed by various agents and temperatures which are innocuous to older cells. Hegarty<sup>7</sup> has found that cells from mature cultures of streptococci cannot act on certain sugars unless they have grown in contact with them. Cells in the period of "physiological youth" can attack these sugars with little or no delay. This adaptation

<sup>1</sup> Abramson, *Electrokinetic Phenomena*, Chemical Catalog Co., New York, 1934.

<sup>2</sup> Abramson, Moyer, and Voet, *J. Am. Chem. Soc.*, 1936, **58**, 2362.

<sup>3</sup> Abramson and Moyer, *Trans. Electrochem. Soc.*, 1937, **71**, 135; Moyer, *ibid.*, 1938, **73**, 481.

<sup>4</sup> Moyer, *J. Biol. Chem.*, 1938, **122**, 641.

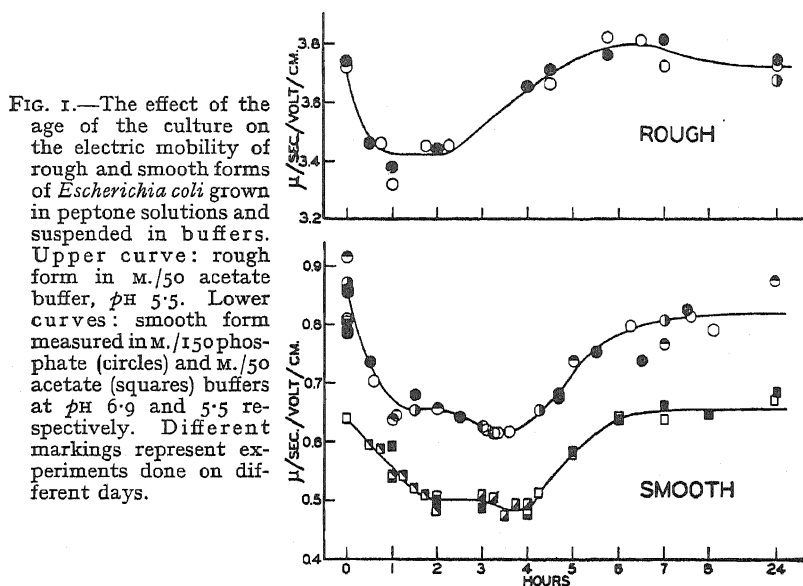
<sup>5</sup> Moyer, *J. Bacteriol.*, 1936, **31**, 531.

<sup>6</sup> Schultz and Ritz, *Cbl. Bakt.* I, 1910, **54**, 283; Reichenbach, *Z. Hyg.*, 1911, **69**, 171; Salter, *J. Inf. Dis.*, 1919, **24**, 260; Sherman and Albus, *J. Bacteriol.*, 1923, **8**, 127; 1924, **9**, 393; Sherman and Cameron, *ibid.*, 1934, **27**, 341; Stark and Stark, *ibid.*, 1929, **18**, 333; Heiberg, *Z. Hyg.*, 1932, **114**, 425.

<sup>7</sup> Hegarty, *J. Bacteriol.*, 1939, **37**, 145.

is most rapid at the end of the lag phase. During the logarithmic phase it decreases in rate. An increased metabolism has also been reported during this early stage, but this aspect of the subject has produced conflicting reports.<sup>8</sup> Shibley<sup>9</sup> has found an altered electric mobility during the first hours of growth, while Pedlow and Lisse,<sup>10</sup> among others, were unable to detect any change. It should be stated, however, that most of these measurements had been made by suspending the cells in distilled water, a medium unsuited<sup>5, 11</sup> for electrophoresis measurements of bacteria because of its lack of buffering power and low and variable ionic strength. In many cases cylindrical cells were employed without adequate control of the field strength or determination of the true stationary levels because of optical effects arising from the curvature of the glass.<sup>12</sup>

When cells of a smooth, non-motile strain of *Escherichia coli* were washed and suspended in buffer solutions it was found that the surface



factors which determine their electrophoretic mobility in mature cultures were constant during long periods of cultivation, provided rough variants had been eliminated.<sup>11</sup> Rough and smooth forms retained their individuality of electrophoretic behaviour even in mixed cultures. If these cells were grown in peptone broth under controlled, aerated conditions, a definite change in the electric mobility was found to occur during the growth cycle. From the time of inoculation until about one hour later, a sharp decrease in the electric mobility was observed (Fig. 1). This decrease in the mobility persists, under our conditions, from about the first hour until the third or fourth hour, whereupon there occurs an increase in mobility back to the original mobility of the cells

<sup>8</sup> For literature, cf. Huntington and Winslow, *J. Bacteriol.*, 1937, 33, 123; Hershey and Bronfenbrenner, *J. Gen. Physiol.*, 1938, 21, 721.

<sup>9</sup> Shibley, *J. Exp. Med.*, 1924, 40, 453.

<sup>10</sup> Pedlow and Lisse, *J. Bacteriol.*, 1936, 31, 235.

<sup>11</sup> Moyer, *ibid.*, 32, 433.

<sup>12</sup> Henry, *J. Chem. Soc.*, 1938, 997.

in the culture used for inoculation. Although the mobility of cells from rough cultures was some six hundred per cent. higher than those from smooth cultures, both types passed through a minimum in electric mobility in the early stages of their culture cycles. Special precautions were taken to eliminate possible flagellar antigens, gases, adsorption from the culture medium, and injury, but the change in mobility was always observed. In several experiments cells were centrifuged and re-suspended in fresh peptone broth. Electrophoresis measurements were then performed. It was found that here, too, the older cells had a higher mobility than the younger. One of the advantages of the microscopic method is that it permits one to observe slight differences by investigating a mixed suspension. When this was done, it was found that young cells, washed and suspended in the same buffer solution with washed older cells, were significantly lower in their mobility than the older cells.

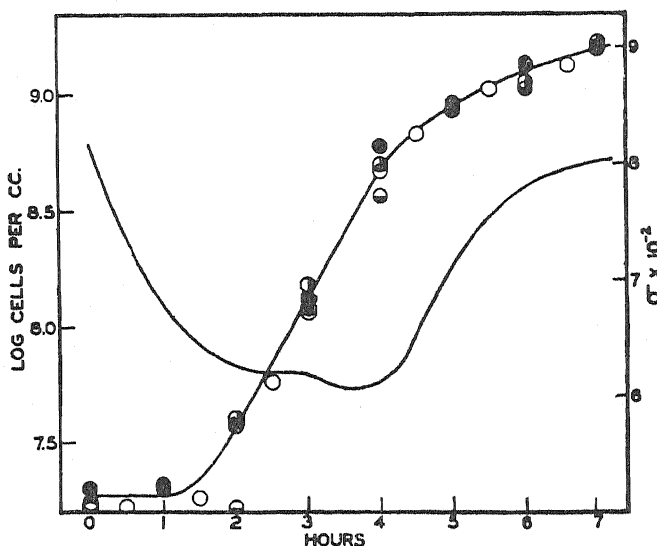


FIG. 2.—Comparison of the growth curve of *Escherichia coli* (smooth) in peptone with the mean charge density-age curve. Different circles represent plate counts made on different days.

Calculation of  $\sigma$ , the net charge density,<sup>11</sup> gave support to the theory of Gouy<sup>1</sup> by revealing that, when the effects of differences in the thickness of the double layer are eliminated, the charge density of *E. coli* is the same, within the limits of error, although suspended in different buffers at two different ionic strengths. In Fig. 2 a comparison is presented between the growth curve for *E. coli* (smooth) under these conditions and the mean charge density-age curve. It will be noticed that the decrease in charge density takes place during the lag phase. This is when the cells are increasing in size with but little division. During the logarithmic period of growth, the curve remains almost constant, although marked changes in the size of the cells take place due to cell division. If size alone were operative in producing these changes in mobility, it might have been expected that striking changes in mobility would have occurred here, yet no such effects were noted. The ionic strength was sufficiently high so that these organisms migrate independently of size or shape. As the period of negative growth acceleration sets in at four hours, the charge density curve slowly rises to

become parallel to the growth curve, until at seven hours both have flattened out to a plateau. This period of decreased mobility corresponds to the period of physiological youth and indicates that actual changes in the physical or chemical constitution of the bacterial surface can occur during the culture cycle. Watrous<sup>13</sup> has presented measurements which also show changes in the mobility of typhoid organisms with the age of the culture.

### Latex Particles and Plant Relationship.

Numerous attempts have been made by botanists to demonstrate chemical relationships between species. It occurred to me that latex, the milky juice found in many plants, might be used to characterise the plants and provide a means for showing physico-chemical relationships. It is generally agreed that the colloiddally dispersed rubber particles in latex are frequently coated with proteins and that they are contained within living cells.<sup>14</sup> It was found<sup>15</sup> that latex particles from various species of *Euphorbia* (spurge) and *Asclepias* (milkweed) exhibit definite electrophoretic mobilities which are functions of the  $pH$  of the buffer in which they are investigated. The isoelectric point of latex particles from any individual plant in a species was constant within 0.1  $pH$  unit. This constancy appears to depend only upon the species and not upon environmental differences, when the plants are in healthy condition.<sup>16</sup> Fresh latex was always used. Electrophoretic mobility- $pH$  curves for the latex particles of the same species from different sources were identical within the limits of error. When curves of similar shape were grouped,<sup>15</sup> it was found that these families of curves agreed with the taxonomic arrangements already established for the genera. As an example of a typical group, Fig. 3 is presented to show the behaviour of latex particles from species in the rough-seeded Galarrhaei section of *Euphorbia*. Notice that the curves are similar in shape and that the breaks in the lines occur at nearly the same  $pH$  value in each of the four. The isoelectric points lie between  $pH$  3.3-3.4. It is interesting to notice the close agreement between *E. verrucosa* and *E. verrucosa* var. *velutina* (hitherto unpublished). When these investigations were started, *E. verrucosa velutina* was tentatively called *E. Welwitschii* from the name on the seed envelope. It seemed strange that the mobility curves and isoelectric point showed such good agreement between this form and *E. verrucosa*. A careful identification of specimens of "*E. Welwitschii*" revealed them to be *E. verrucosa velutina* and the close similarity was explained. Numerous other such groups of curves are presented in the original communications.<sup>15</sup>

A similar discrepancy was noted in the section Poinsettia.<sup>17</sup> Although the poinsettias agreed in their electrophoretic behaviour for the most part, *E. heterophylla* was quite different in its curve shape and isoelectric point. No published taxonomic evidence could be found to justify this anomalous behaviour. When its chromosomes were counted, however, it was discovered that *E. heterophylla* was polyploid with a chromosome number of 56, whereas the other poinsettias investigated had chromosome numbers of 28.

<sup>13</sup> Watrous, *J. Inf. Dis.*, 1937, 60, 47.

<sup>14</sup> Moyer, *Bot. Review*, 1937, 3, 522.

<sup>15</sup> Moyer, *Am. J. Bot.*, 1934, 21, 293; *Bot. Gaz.*, 1936, 97, 860.

<sup>16</sup> Moyer, *Protoplasma*, 1934, 21, 588.

<sup>17</sup> Moyer, *Bot. Gaz.*, 1934, 95, 876.

The relatively high position of the isoelectric points of the latex particles of many of these species indicated that the surfaces were often composed of proteins. The numerous points of inflection observed in certain of the curves suggested that some of the surfaces were composed of mixtures of proteins or of proteins with sterols or similar substances. In some species the surfaces were undoubtedly non-protein in nature. This was confirmed by an investigation of the wetting properties of these latex particles.<sup>18</sup> Measurements of the electrophoresis of sterols<sup>19</sup> produced curves for ergosterol and cholesterol

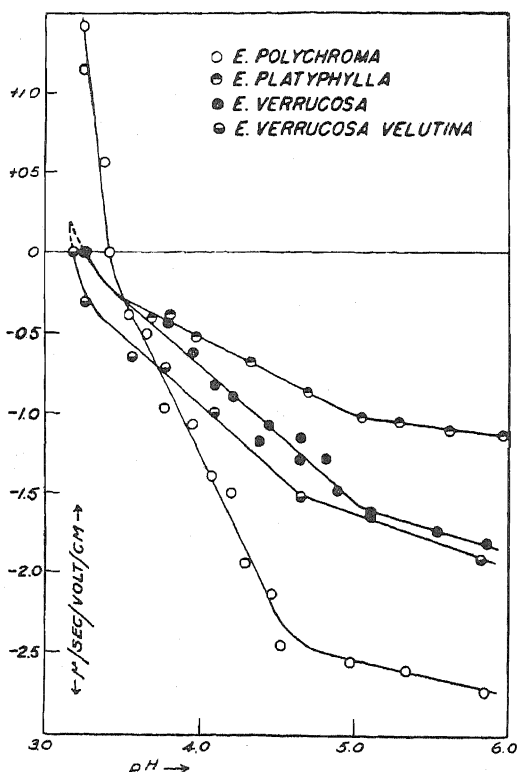


FIG. 3.—The electric mobility-pH curves of latex particles from closely related *Euphorbia* species in M./50 acetate buffers at 25°.

particles of *Hevea*. As Bondy and Freundlich point out, this latex curve is similar to several of my own obtained with *Euphorbia* latex.

### The Nature of the Active Principle in Ragweed Pollen.

It is a fortunate circumstance that quartz or other inert particles when placed in dilute solutions of protein become coated with a film of the protein and assume an electric mobility close to or identical with

<sup>18</sup> Moyer, *Am. J. Bot.*, 1935, **22**, 609.

<sup>19</sup> Moyer, *Biochem. Z.*, 1934, **273**, 122; *J. Gen. Physiol.*, 1935, **18**, 749; 1935, **19**, 89.

<sup>20</sup> Bondy and Freundlich, *Compt. rend. trav. lab. Carlsberg*, 1937, **22**, 89.

that possessed by the protein in the dissolved state.<sup>1, 21</sup> Such particles may be investigated by the microscopic method and have been found to move independently of size and shape.<sup>1</sup>

By suspending particles of quartz, collodion, and mineral oil in dialysed aqueous extracts of ragweed pollen (*Ambrosia trifida*), Abramson, Sookne and the author<sup>22</sup> found that these quartz particles had now become amphoteric in behaviour with an isoelectric point at  $pH$  4.3 (Fig. 4). The high position of the isoelectric point on the  $pH$  scale,

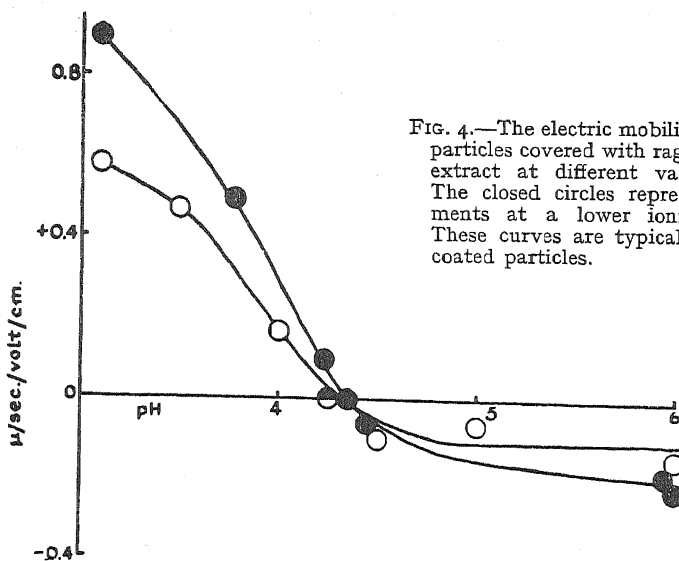


FIG. 4.—The electric mobility of quartz particles covered with ragweed pollen extract at different values of  $pH$ . The closed circles represent experiments at a lower ionic strength. These curves are typical of protein-coated particles.

together with the shapes of the electric mobility and titration curves of the dialysed extract suggested that these particles had assumed protein films. Mineral oil and quartz particles, although having widely different electric mobilities, when placed in these pollen extracts became identical in electrophoretic behaviour, within the limits of error. When quartz particles were added to dilute extracts of ragweed pollen and centrifuged, the extracts became partially or wholly inactivated and no longer yielded positive scratch tests on the arms of subjects allergic to this pollen. From this evidence it was concluded that the quartz adsorbs the active principle which is probably a protein substance.<sup>23</sup>

### The Behaviour of Inert Particles when Suspended in Serum.

Tiselius<sup>24</sup> and Stenhagen<sup>25</sup> have shown that horse and human serum contain components belonging to the globulin and albumin fractions which can be isolated by the method of electrophoretic analysis.

<sup>21</sup> Moyer, *Cold Spring Harbor Symposia on Quant. Biol.*, 1938, 6, 228; Abramson, Gorin and Moyer, *Chem. Reviews*, 1939, 24, 345.

<sup>22</sup> Abramson, Sookne and Moyer, *J. Allergy*, 1939, 10, 317.

<sup>23</sup> Abramson has recently discovered that timothy and ragweed pollen extracts can be transported into the intact skin by electrophoresis. Four cases of hay fever have been treated by this means with promising results (Abramson, *N.Y. State J. Med.*, 1939, *in press*).

<sup>24</sup> Tiselius, *Biochem. J.*, 1937, 31, 1464.

<sup>25</sup> Stenhagen, *ibid.*, 1938, 32, 714.



In respect to electric mobility, the isolated constituents agree closely with these substances in diluted serum. Just as the moving boundary method is capable of investigating these different constituents of serum, although in the natural, mixed state, the microscopic method can also be made to reveal certain components in normal serum. It has been found by Abramson<sup>26</sup> that quartz particles and mineral oil droplets when placed in highly diluted human or rabbit serum changed markedly in their electric mobilities and became constant and very similar in behaviour at a serum dilution of 1:10,000. He found that this uniformity of surface was retained between 1:10,000 to 1:50 dilution of serum. No significant differences were found between the mobility-*pH* curves of serum-coated quartz particles and mineral oil droplets over the range, *pH* 3.5-6.0 in NaCl-acetate solutions. The behaviour of these coated particles is especially interesting because of the fact that both horse serum albumin and pseudoglobulin exhibit little or no change in

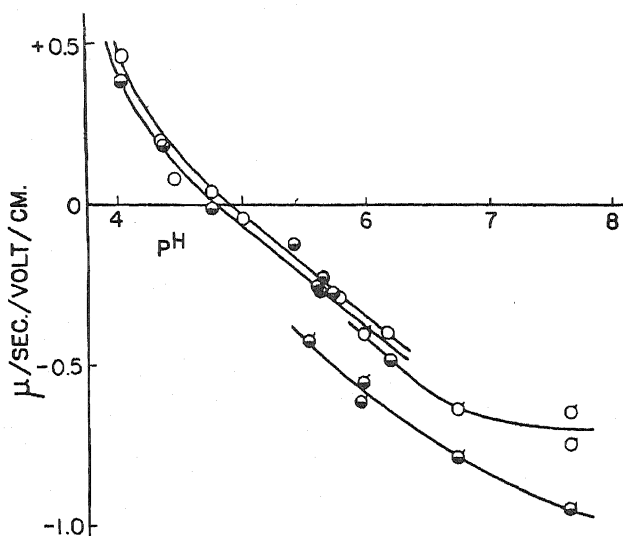


FIG. 5.—The electric mobility at 25° of collodion (○) and quartz (●) particles in 1:50 dilutions of normal rabbit serum at a constant ionic strength of 0.1. The tagged circles were measured in phosphate buffers, the others in acetate.

their acidic and basic groups on adsorption as indicated by the constancy of the electric mobility and the isoelectric point in the adsorbed and dissolved states.<sup>21</sup> It is possible, therefore, that these curves may indicate the behaviour of the serum proteins in the dissolved condition.

The present experiments deal with the electric mobility of quartz and collodion particles placed in 1:50 dilutions of rabbit serum in the presence of acetate or phosphate buffers at a constant ionic strength of 0.1. Particles were placed in the undiluted normal serum and after sufficient time had elapsed to produce a complete coating, the buffer constituents were added and the mixture diluted to the desired concentration. It will be noticed in Fig. 5 that the results in acetate buffers are similar to the findings of Abramson with human serum, for little if any significant difference could be found between the behaviour of quartz or collodion. A slight difference in the isoelectric points was observed but the low mobility and high ionic strength prevented the determination of their exact positions except by interpolation. They lay near

<sup>26</sup> Abramson, *J. Gen. Physiol.*, 1929, 13, 169.

pH 4.8-4.9. If, however, the particles were suspended in serum in phosphate buffers at the same ionic strength (indicated by the tagged circles), striking differences in the behaviour of the collodion and quartz particles were at once apparent. Evidently the nature of the surface films formed on these particles is quite different. The quartz seems to adsorb an albumin while the collodion appears to become coated with a globulin. It will be noticed that there is a distinct break between the acetate and phosphate curves, caused by the difference in ionic species. The film adsorbed by the collodion is much less affected in this respect than is the coating of the quartz. It seems probable that this behaviour should be ascribed to differences in the adsorption of ions by the proteins composing the surfaces, for the curves are shifted bodily without much change in slope. Shifts of this character have been discussed by Abramson<sup>27</sup> and by Abramson, Gorin and myself.<sup>21</sup> Thus it appears that even though the mobility of the coated quartz and collodion particles is nearly identical in acetate buffers, the chemical nature of the films involved may be quite different.

Another instance where differences in constitution may be masked by an apparent identity in electrophoretic mobility is shown in the case of the serum albumins isolated by Kekwick.<sup>28</sup> Kekwick has found two crystalline albumins in horse serum. Albumin A is yellow with small crystals and a higher carbohydrate content than the colourless, more insoluble albumin B which has large crystals. Albumin A was found to be serologically different from albumin B.<sup>29</sup> Both proteins have identical sedimentation constants, molecular weights, and electrophoretic mobilities (at  $\mu = 0.02$ ) in the pH range 4.2-5.5, within the limits of error.

Kekwick's electrophoresis data have been shown<sup>21</sup> to be in excellent agreement over this pH range with the data of Tiselius<sup>30</sup> (who also used the moving boundary method) and with the data of Abramson<sup>31</sup> and Moyer<sup>4</sup> for serum albumin adsorbed on microscopic particles. No attempt was made by Abramson or myself to fractionate our serum albumin preparations.

Serum albumins A and B were crystallised from  $\text{Na}_2\text{SO}_4$  solutions by Kekwick's method. Albumin preparations were obtained which agreed in crystal size, colour, and solubility with those described by Kekwick. The same procedure was used to crystallise the albumins from another sample of horse serum from a different source with the same result. The electric mobility-pH curves given by these fractions when adsorbed on quartz or collodion particles are shown in Fig. 6. No difference could be noticed between the behaviour of quartz or collodion particles in contact with either of the purified proteins. Both albumin curves were identical over the pH range investigated by Kekwick, consequently measurements in this region do not permit one to decide which of the two proteins is being measured. It will be noticed that the curves diverge definitely at either end of this range, indicating that, except for a narrow region near the isoelectric point (pH 4.75 at this ionic strength), the two proteins exhibit a different electrophoretic behaviour. The open circles are the data of Moyer and Abramson<sup>32</sup> for serum albumin at this ionic strength. Evidently we were dealing

<sup>27</sup> Abramson, *J. Gen. Physiol.*, 1933, **16**, 593.

<sup>28</sup> Kekwick, *Biochem. J.*, 1938, **32**, 552.

<sup>29</sup> Gell and Yuill, *ibid.*, 560.

<sup>30</sup> Tiselius, *Nova acta reg. soc. sc. Upsaliensis*, 1930, **7**, no. 4.

<sup>31</sup> Abramson, *J. Gen. Physiol.*, 1932, **15**, 575.

<sup>32</sup> Moyer and Abramson, *J. Biol. Chem.*, 1938, **123**, 391.

with albumin B. All preparations agreed in isoelectric point. In harmony with previous findings,<sup>4, 24</sup> no definite shifts were noticed in the curves on changing the buffer system from phosphate to acetate (near pH 6), providing the ionic strength was kept constant at 0.1. Measurements of quartz particles suspended in diluted horse serum indicate that serum albumin A is adsorbed exclusively by the quartz from the serum.<sup>33</sup> Titration curves of these two proteins should bear the same relationship to each other as the electric mobility curves in view of the identity of the diffusion and sedimentation constants.<sup>1, 21, 31, 32, 34</sup>

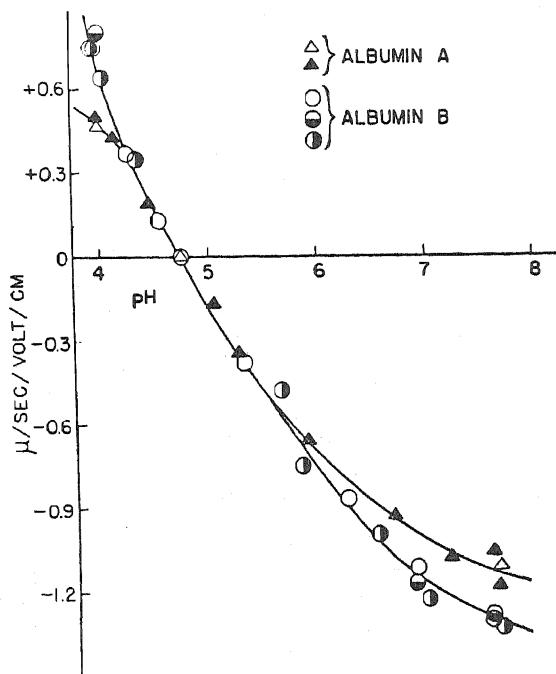


FIG. 6.—The electric mobility of solutions of the crystalline serum albumins A and B prepared by Kekwick's method when coated on quartz or collodion particles at  $\mu = 0.1$  and  $25^\circ$ .

### Conclusion.

It is hoped that these results will serve to emphasise the value of applications of electrokinetic phenomena to biological problems. It is expected that other papers in this symposium will discuss the exceedingly important data secured with the modern techniques now available in the fields of protein chemistry and immunology. Many other topics which cannot be discussed here have been presented elsewhere.<sup>1, 3, 21</sup>

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<sup>33</sup> Unpublished observations.

<sup>34</sup> Moyer and Abels, *J. Biol. Chem.*, 1937, **121**, 331.

# THE ELECTRICAL DOUBLE LAYER AND VIRUS STABILITY.

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The discovery in recent years of effective methods of isolating and purifying animal and plant viruses has afforded new opportunities of examining their behaviour. It has also provided for purposes of investigating certain principles and formulæ in colloidal chemistry homogeneous colonies of particles in an interesting size range, *viz.*, larger than the molecules of the more familiar proteins and yet below the limits of microscopic visibility.

## General.

More exact information is available about the physical properties of the plant viruses than of the animal viruses. This is mainly due to the stimulus deriving from the crystallisability of these viruses and to the accuracy of the crystal measurements thereby made possible. In general, the plant viruses are nucleo-proteins with rod-shaped molecules, typical dimensions being  $15.2\text{m}\mu$  for the effective thickness of the tobacco mosaic virus<sup>1</sup> and 35-40 times this value for the length.<sup>2, 3</sup> A notable exception to the asymmetrical shape is shown by Bushy stunt virus which crystallises in the cubic system,<sup>4</sup> and for which a diameter of  $13.7\text{m}\mu$  for the spherical molecule has been calculated.<sup>5</sup> Much has been written about the sizes of the animal viruses, but until many of these are available in purer form and more is known about the particle shape it is probably only safe to say that they cover a wide range from dimensions of the order of those of the plant virus "molecules" up to microscopic visibility.

One animal virus in particular has been the subject of much recent investigation, *viz.*, the virus of vaccinia, and it is proposed to discuss here in detail some of the stability relationships of it. It is prepared<sup>6</sup> by scraping the characteristic lesions on the infected rabbits' back whereby a pulp of pustular material and skin debris is obtained. From this the virus is extracted in the form of a milky suspension in dilute salt solution. The virus particles are large enough (approx.  $200\text{m}\mu$  in diameter) to be visible by dark-ground illumination and give an impression of considerable uniformity in size (Fig. 2). There is now no doubt, that these particles alone are the causal agent of the disease, no significantly smaller particles having been found capable of exercising this function whether obtained by disintegration of these particles or from any other source. The virus particles sediment rapidly in centrifugal fields of only 1000 times gravity and the sedimentation boundaries show some progressive blurring with time (Fig. 1, Plate II),.

<sup>1</sup> F. C. Bawden, N. W. Pirie, J. D. Bernal and I. Fankuchen, *Nature*, 1936, 138, 1051.

<sup>2</sup> V. L. Frampton and H. Neurath, *Science*, 1938, 87, 468.

<sup>3</sup> M. Lauffer, *ibid.*, 469.

<sup>4</sup> F. C. Bawden and N. W. Pirie, *Brit. J. Exp. Path.*, 1938, 19, 251.

<sup>5</sup> A. S. McFarlane and R. A. Kekwick, *Biochem. J.*, 1938, 32, 1607.

<sup>6</sup> J. Craigie, *Brit. J. Exp. Path.*, 1932, 13, 259.

### Stability of Protein Suspensions.

The stability in aqueous suspension of colloidal particles of any kind, is due to three main factors, *viz.*, hydration of ionising groups, hydration of non-ionising polar groups, and hydration associated with the adsorption of salt ions in the form of the diffuse double layer. It is not implied that there is a rigid distinction in principle between these three methods of holding water to the colloidal particle, the identification of the three types of hydration being a practical one justified by its usefulness in analyses of the causes of suspension stability. It has been recognised for some time in the case of protein solutions that polar hydration plays a major part in determining their stability. Non-polar hydration is also of importance in the case of proteins (*e.g.*, egg albumin, hæmoglobin) which are soluble at the isoelectric point, but in the case of the globulins, it is of little significance.

The electrophoretic mobility depending as it does on the total potential difference between the particle and the stationary medium is a measure both of the ionisation potential and of the potential associated with the double layer. The work of Abrahamson<sup>7</sup> and Moyer<sup>8</sup> suggests that the mobility of the proteins is accounted for solely by the ionisation potential and consequently that the adsorption of salt ions must be negligible in amount. Their evidence rests on a proportionality of acid-base binding capacity and mobility in the cases of egg albumin,<sup>9</sup> serum albumin and pseudoglobulin.<sup>10</sup> It is known that certain polyvalent ions exert specific effects on proteins, and Abrahamson and Moyer's conclusions are, therefore, expressly limited to "protein solutions containing only simple electrolytes which do not form protein complexes."<sup>11</sup> Even with this important limitation it is doubtful whether the absence of simple ion adsorption can be a general phenomenon. Adair and Adair,<sup>12</sup> using measurements of membrane potential to determine the isoelectric point of hæmoglobin, find evidence of selective binding of buffer ions in varying ionic concentrations of ammonium phosphate. They also show that there is a significant difference between the isoelectric and isoionic points and that differences are detectable in the iso-electric point depending on whether the buffer cations are sodium or ammonium, and the anions chloride or phosphate. Tiselius<sup>13</sup> also finds specific buffer ion effects on the isoelectric point, and the slope of the *pH*-mobility curve, and is unable to correlate the mobility of egg albumin solutions with the acid-base binding capacity. However, whether or not one accepts the view that protein mobility is exclusively determined by the ionisation of acidic and basic groups it is clear that this is a much more important factor in protein stability than an adsorption potential.

### Stability of Cells and Bacteria.

In contrast to the proteins which are to be classed as lyophilic substances, the behaviour of bacterial and cell suspensions shows a greater resemblance to that of the lyophobic sols. Precipitation of a protein from solution, whether by changing the *pH*, by addition of salts, by drying, and other agencies is generally followed by rapid solution when the conditions are reversed. On the other hand the re-constitution of the diffuse ion atmosphere of a metallic sol, once flocculation has occurred is always

<sup>7</sup> H. A. Abrahamson, *Electrokinetic Phenomena*. The Chemical Catalog. Co. Inc., New York, 1934.

<sup>8</sup> L. S. Moyer, *Cold Spring Harbor Symposia Quart. Biol.*, 1938, 6, 228.

<sup>9</sup> L. S. Moyer and J. C. Abels, *J. Biol. Chem.*, 1937, 121, 331.

<sup>10</sup> L. S. Moyer and H. A. Abrahamson, *ibid.*, 1938, 123, 391.

<sup>11</sup> H. A. Abrahamson, M. H. Gorin and L. S. Moyer, *Chem. Rev.*, 1939, 24, 345.

<sup>12</sup> G. S. Adair and M. E. Adair, *Biochem. J.*, 1934, 28, 1230.

<sup>13</sup> A. Tiselius, *Nova Acta Regiae Soc. Sci. Upsaliensis*, 1930, 7, No. 4.

a slow and difficult process, and in many instances has not been realised. The same is true of bacterial flocculation from any cause. It is possible that a series of irreversible changes follows bacterial flocculation, but there is no experimental evidence for this, the infectivity being unchanged, and no obvious reason why this should characterise bacteria, which are mainly protein in nature, and be conspicuously absent in the soluble proteins. Another characteristic of the lyophobic system, *viz.*, flocculation in relatively low concentrations of univalent salts, or in the presence of traces of polyvalent ions of opposite sign of charge to the particle, is characteristic of the cellular group and is exhibited to a smaller extent or not at all in the case of the soluble proteins. In common also with the metallic sols. bacteria and cells may frequently be agglutinated by freezing, whereas protein solutions are characteristically unaffected by this treatment.

There is thus evidence that cell suspensions like metallic solutions are dependant mainly on an adsorption potential rather than an ionisation potential for their stability. It is difficult to exclude the possibility however, that part of the  $\xi$ -potential is contributed by ionisation of acidic or basic groups. The red cell for example, has a definite ionisation potential, but this is to be expected in view of its highly specialised function in maintaining the acid-base balance of the blood. It does not appear consistent with the natural economy to endow the surfaces of cells intended for an independent existence with numbers of ionogenic groups. This question is difficult to settle by titration experiment since the amount of ionising protein forming the surface layer of the cell may be very small.

The question which naturally arises is to what extent are the differences in the stability behaviour of protein molecules and cells merely due to differences in particle size, and to what extent are they due to more specific considerations, such as the presence of a semi-permeable membrane. The study of an intermediate size group in the viruses may throw some light on this.

### Virus Stability.

The plant viruses behave in respect of most of their stability properties as typical soluble proteins being precipitated by high concentrations of salt and easily re-dissolved again in water. In one property they are atypical, however. The anisotropic members show a zone of aggregation somewhere in the range  $pH$  2 to 6. Inside this zone, which includes the isoelectric point, they sediment rapidly and may readily be concentrated by means of a laboratory centrifuge. In the absence of mobility data it is not possible to offer an explanation of the stability conditions of these aggregates. By contrast, proteins which are insoluble at the isoelectric point aggregate rapidly and form a precipitate. A third and unusual type of aggregation is seen in the case of casein particles which show a continuous and reversible aggregation on addition of calcium ions.<sup>14</sup> Approximately homogeneous suspensions of differing grades of dispersity are obtained which are stable so long as the  $pH$  and calcium ion concentration are maintained. The isotropic Bushy stunt virus exhibits no zone of aggregation and is quite soluble at the iso-electric point.

The behaviour of vaccinia virus is in sharp contrast to the plant viruses. Suspensions of the virus are only stable for a few days at room temperature, and for a few weeks if kept in the cold. Inevitably a flocculum is found at the bottom of the tube leaving a clear supernatant fluid. This flocculation is accelerated by addition of small quantities of salts and takes place in 24 hours in  $M/10$  sodium chloride. The virus is prepared and kept in a neutral or slightly alkaline medium, and is, therefore, always negatively charged. Flocculation takes place rapidly on contact with traces of polyvalent cations. It occurs instantaneously on freezing; and at  $pH$ 's

<sup>14</sup> J. St. L. Philpot, *Proc. Roy. Soc., A*, 1939, 170, 60.

below 5.5.<sup>15</sup> It also occurs on repeated washing or dialysis against distilled water and is not due in this case as one might expect to membrane hydrolysis since the  $pH$  of the medium is still above 6 when flocculation takes place.

Fig. 2 (Plate II) shows the dark-ground microscopic appearance of vaccinia floccules obtained by simple drying. Until recently it was believed that flocculation of the virus from any of the causes mentioned is irreversible. It has been shown<sup>16</sup> that the virus particles possess a surface layer of lipid the presence of which makes redispersion of the virus particles a difficult matter. This lipid may be extracted from the dried virus by ether or benzene, and the resuspension of the virus particles is then obtainable by slow grinding of the floccules between close-fitting cylindrical glass surfaces in the presence of favourable conditions for the formation of an ion atmosphere, *viz.*, in a very dilute solution of univalent cations of  $pH$  8.0. The dried and resuspended virus has the same dark-ground appearance as the original, gives identical sedimentation pictures, and has lost none of the original infectivity. The resuspension has recently been obtained in a rapid and quantitative manner by the use of ultra-sonic vibrations.<sup>17</sup> The dry virus powder may be left in contact with the dilute buffer for months without any signs of spontaneous resuspension taking place.

A broad consideration of these properties of the virus reveals a striking similarity to the lyophobic sols. It can scarcely be doubted that the virus depends mainly for its stability on an adsorbed double layer which is destroyed by freezing, by drying, by salts in moderate concentration or of high valency, and by washing to remove the minimum of electrolytic necessary to maintain the potential above the flocculation threshold.

### Electrophoresis of Viruses.

In Fig. 3 (Plate III) (b) are shown photographs of the migrating boundary of Bushy stunt virus in the Tiselius apparatus. The internal width of the U-tube is 3 mm. and no evidence of endosmosis at the walls is visible. The mobility in the experiment illustrated is  $4.75 \times 10^{-5}$  cm./sec. at  $pH$  6.3 in 0.02 M. acetate buffer. Fig. 3 (a) is from an experiment on vaccinia virus in the same apparatus, and shows that in this case marked endosmotic streaming has taken place. A fine track of virus is to be seen extending down the centre of the tube. In the opposite limb of the U-tube the picture is reversed, a thin stream of buffer running down into the virus suspension with marked cusping at the meniscus. The mobility of vaccinia in phosphate buffer of ionic strength  $\mu = 0.05$  and  $pH$  7.0 is approximately  $10 \times 10^{-5}$  cm./sec. as nearly as can be estimated in the presence of the endosmotic disturbance, and there is only a small variation with  $pH$  in this region. Variations in  $pH$  or ionic strength do not significantly affect the endosmotic flow, which is present both in suspensions of native virus and virus which has been dried, extracted with ether and resuspended in the manner described. It appears to be an inevitable accompaniment of the migration, and one of great practical significance since its presence frustrates effectively attempts at electrophoretic separation of non-infective fractions from the crude tissue extract.

The flat boundary shown by Bushy stunt is typical of the boundaries shown by most soluble proteins in the Tiselius apparatus, some having mobilities as high or higher than the value obtained for vaccinia. There seems therefore to be an essential difference between the behaviour of

<sup>15</sup> J. W. Beard, H. Finkelstein and R. W. G. Wyckoff, *J. Immunol.* 1938, **35**, 415.

<sup>16</sup> A. S. McFarlane and M. G. Macfarlane, *Nature*, 1939, **144**, 376; also A. S. McFarlane, M. G. Macfarlane, C. R. Amies and G. H. Eagles, *Brit. J. Exp. Path.*, 1940, **21**.

<sup>17</sup> F. H. Hopwood, M. H. Salaman and A. S. McFarlane, *Nature*, 1939, **144**, 377.

ordinary proteins and vaccinia and several explanations suggest themselves. It is possible that the molecules of most of the proteins do not adhere to the walls of the U-tube. The work of Langmuir and his associates<sup>18</sup> shows that the surfaces of metal plates require to be prepared in various ways before they will pick up protein mono-layers. Moyer and Abrahamson appear to have no difficulty in covering quartz and collodion particles with protein layers but there is evidence that here also individual variations occur. Their finding that the mobility of quartz particles coated with serum albumin is exactly the same as the mobility of this protein in solution and equal and apposite to the endosmotic current at the walls of the chamber suggests that in all three cases the globular molecule is undeformed and that the surface layer consists of molecules lightly adhering to the substratum. Egg albumin on the other hand has a different mobility and different isoelectric point in solution and when layered on quartz.<sup>19</sup> This protein readily forms true mono-layers 10 Å. in thickness,<sup>20</sup> the presence of an oriented layer on the surface of a purified egg albumin solution being self-evident in a rigidity of the surface which is not noticeable with other proteins. Solutions of this protein also denature readily on shaking. Whether the film is denatured or not<sup>21</sup> it is evident in the course of mono-layer formation that extensive changes in intra-molecular distances must occur affecting the dissociation of ionising groups. These facts appear to explain in part at least the difference in the behaviour of serum albumin and egg albumin. One may therefore visualise three possible states at the inert surface of an electrophoresis tube containing a protein solution, *viz.*, (1) true monolayer formation, requiring a protein which spreads readily; (2) formation of a film of adhering, but otherwise undeformed protein molecules; and (3) no association of molecules with the surface. In the first two cases endosmotic streaming will occur, but in different degree, and in the third the migrating boundaries will be flat. In the case of vaccinia the evidence is in favour of the view that the endosmosis is due to virus particles adhering lightly to the walls of the tube. This virus does not deform on the surface of a spreading trough<sup>22</sup> and dark-ground observations show that the particles have a marked tendency to adhere to glass surfaces in an apparently undeformed state. This is also true of the virus particles after drying and extraction of surface lipid. It appears therefore that in normal working conditions the molecules of soluble proteins in general may not associate with the wall of the Tiselius U-tube whereas vaccinia particles do.

An alternative explanation is that endosmosis is present in the case of the soluble proteins but to an extent which we fail to observe owing to the smallness of the molecules themselves and to the fact that the effective thickness of the ion atmosphere must be small in buffers of the ionic strength commonly used. If this were the case, however, one would expect to find some evidence of endosmosis with molecules as large as those of Bushy stunt instead of an abrupt transition from perfectly flat boundaries to the grossly distorted vaccinia boundaries.

Attention has already been drawn to the fact that the sedimentation pictures of vaccinia (Fig. 1) show somewhat blurred boundaries. Careful studies of many vaccinia preparations by Pickels and Smadel<sup>23</sup> show that the degree of boundary spreading is approximately 14 per cent. Differences of 14 per cent. in sedimentation constant, assuming that these are due entirely to difference in particle weight, correspond to differences of only 2½ per cent. in any linear dimension, which supports the apparent uniformity

<sup>18</sup> I. Langmuir and V. J. Schaefer, *Chem. Rev.*, 1939, **24**, 181.

<sup>19</sup> E. R. B. Smith, *J. Biol. Chem.*, 1936, **113**, 473.

<sup>20</sup> E. Gorter, J. van Ormondt and F. J. P. Dom, *Proc. Kon. Akad. v. Wet.*, 1932, **35**, 838.

<sup>21</sup> H. B. Bull and H. Neurath, *J. Biol. Chem.*, 1937, **118**, 163.

<sup>22</sup> J. Seastone, *J. Gen. Physiol.*, 1938, **21**, 621.

<sup>23</sup> E. G. Pickels and J. E. Smadel, *J. Exp. Med.*, 1938, **68**, 583.



in particle radii revealed by the dark-ground microscope. Nevertheless, it is possible that an even higher degree of size-homogeneity exists and that the blurring of the sedimentation boundaries is due to endosmosis occurring at the transparent walls of the centrifuge cell and caused by the potential which must be set up in the fluid by the sedimentation of charged virus particles. Since sedimentation is usually rapid and is frequently observed in media of low ionic strength the potential between the bottom and the top of the cell may be of the order of 10-30 volts.

### Discussion.

There seem to be no sound reasons for believing that the surface of the vaccinia body is delimited by a semi-permeable membrane. The stability of the virus towards lipid solvents precludes the existence of the familiar type of semi-permeable membrane which is based on a lipid-protein duplex film.<sup>24</sup> The stability of the particle to mechanical treatment is such as cannot readily be attributed to a membrane. No amount of grinding and squeezing is able to liberate a solution of protein. When spread on a water surface the virus particles are not significantly deformed<sup>22</sup> in spite of the enormous surface forces to which they must thus be subjected and which suffice to rend other cells to pieces. The virus can be taken from water into 35 per cent. sucrose or the same concentration of glycerol and back again to water<sup>25</sup> with no evidence of cell disruption. It is intact in 10-15 per cent. urea which hæmolyzes red cells.

Some observers<sup>25, 26, 27</sup> deduce from extrapolation of sedimentation constants in media of different densities that the effective density of the particle is 1.16-1.18 in water, and increases by osmotic dehydration in concentrated sucrose solutions. The evidence for this at the moment is inconclusive. The comparison of sedimentation constants in different media involves the use of viscosity corrections particularly for electroviscous effects for which adequate data is not available. Lauffer<sup>28</sup> has demonstrated the presence of such effects in the case of tobacco mosaic virus. Owing to the ready flocculability of the virus sedimentation measurements are usually made in solutions containing very little electrolyte—of the order of 0.01 to 0.001 M. In these circumstances the  $\xi$ -potential is high and the ion atmosphere must extend a considerable distance from the surface of the virus. It is difficult to predict how much surface water will sediment with the virus particle. It is probable also that different amounts will move with the virus according to the ionic strength of the medium.

Some importance attaches to measurements of the hydration of the virus not merely in their relation to viscosity and density values, but because they may help in deciding between conflicting views on the constitution of the particle, *viz.*, whether it is a highly hydrated cellular structure or a relatively anhydrous mass of protein. Unfortunately the physical differentiation of water held osmotically within a particle of this size and oriented dipoles held electrically within the diffuse double layer is a matter of the greatest difficulty. There are indications that in dilute salt solutions relatively enormous amounts of water are associated

<sup>24</sup> E. N. Harvey and J. F. Danielli, *Biol. Rev.*, 1938, 13, 319.

<sup>25</sup> J. E. Smadel, E. G. Pickels and T. Shedlovsky, *J. Exp. Med.*, 1938, 68, 607.

<sup>26</sup> W. J. Elford and C. H. Andrewes, *Brit. J. Exp. Path.*, 1936, 17, 422.

<sup>27</sup> W. J. Elford in Doerr and Hallauer's *Handbuch des Virusforschung*, Julius Springer, 1938.

<sup>28</sup> M. Lauffer, *J. Biol. Chem.*, 1938, 126, 443.

with the virus particle. If the virus is centrifuged for long periods a packed deposit of almost constant volume is obtained and of this volume only about 1/6th is dry virus substance. The repulsion distances between the particles must therefore be very large. If a little sucrose is added to the suspension before centrifuging almost all of it is found in the supernatant, showing that most of the space between the packed virus particles is not accessible to the sucrose molecules.<sup>29</sup> Addition of electrolyte reduces the volume of the virus deposit and in concentrations of sodium chloride greater than M./30 it is evident that the virus particles begin to carry down the added electrolyte with them. It is impossible for all or a large part of the water thus associated with the virus to be constrained inside a semi-permeable membrane since the size of the resulting cell would be much greater than is known to be the case from ultra-violet photographs.<sup>30</sup> It has also been noted in these experiments that the hydration varies in general with the ionic strength of the medium and not with the osmotic pressure.

Vaccinia virus does not crystallise and the individual particles are not macroscopically crystalline. One might be tempted therefore to infer that it has an amorphous constitution. It has to be borne in mind however that the counterpart of the vaccinia body in the plant viruses is not the Bushy stunt crystal but the Bushy stunt molecule and although these pack into a cubic lattice it does not follow that each molecule is a perfect geometrical replica of every other in the crystal. Experience with other proteins shows indeed that this is not the case. Serum albumin, for example, which crystallises well can be separated into fractions of entirely different solubility.<sup>31</sup> A molecule of serum albumin if we had the means of observing it probably would not appear crystalline. It has as we know from X-ray observation a regularity of structure but not any more so than a hair or a muscle fibre. It is difficult to believe that such a vital and biologically indivisible piece of matter as the virus particle does not also have a regular internal arrangement although an apparently amorphous exterior.

Hartley<sup>32</sup> has pointed out that colloids may conveniently be classed in two groups; those in which the particles are small and in complete equilibrium with the medium, and those in which the bulk of the particle is made up of insoluble material in regard to which there is no equilibrium. The charge in the first group is mainly due to ionisation and the principles developed by Debye and Hückel are applicable; in the second group the charge is due chiefly to preferential adsorption of foreign ions and the  $\xi$ -potential treatment gives more promising results. The proteins appear to fall between the two groups. The molecules of the proteins are large by Hartley's standards and yet on the whole responded well to analyses based on ionic principles. There is good evidence for a chemical equilibrium with the medium and this is due no doubt to a porous or flexible protein structure which is the subject of lively contemporary discussion.<sup>33</sup> In moving up the scale of size however from the plant viruses to vaccinia it is clear from the foregoing that the general properties of ions recede and the properties of surfaces begin to predominate. It is also apparent

<sup>29</sup> A. S. McFarlane, *Proc. Roy. Soc., B*, 1938, **125**, 301.

<sup>30</sup> J. E. Barnard, *Brit. J. Exp. Path.*, 1935, **16**, 129.

<sup>31</sup> E. J. Cohn, *Chem. Rev.*, 1939, **24**, 203.

<sup>32</sup> G. S. Hartley, *Trans. Faraday Soc.*, 1935, **31**, 66.

<sup>33</sup> I. Langmuir and D. W. Wrinch, *Nature*, 1939, **143**, 49. W. L. Bragg, *ibid.*, 73. J. D. Bernal, *ibid.*, 74.

in the case of vaccinia that this predominance of surface properties does not coincide with the appearance of any demonstrable limiting membrane. Is this change then indicative as with inorganic colloids of an insoluble core? It is difficult to believe that nature would choose to pack essentially insoluble protein inside such active structures as viruses. It appears more reasonable to suppose that the apparent lack of equilibrium between the medium and the interior of the virus is due to the slowness of the diffusion processes necessary for full ionic communication with such a large structure. Alternatively, it may be due to steric considerations resulting in a loss of flexibility in the structure of the virus. It is interesting in this connection to note that neither tobacco mosaic nor vaccinia virus will spread on surfaces.<sup>22, 34</sup>

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<sup>34</sup> I. Langmuir and V. J. Schaefer, *J. Amer. Chem. Soc.*, 1937, **59**, 1406.

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## SOME CONSEQUENCES OF THE ELECTRICAL DOUBLE LAYER IN RUBBER TECHNOLOGY.

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The effects of the electrical double layer in connection with rubber manufacturing processes have, in recent years, become of rapidly increasing technical importance.

In the last two decades remarkable developments have occurred in the application of aqueous dispersions of rubber, or of rubber-producing materials. The characteristics of these dispersions are largely dictated by the electrical double layer and adsorbed material associated with it. These aqueous dispersions may be of several distinct types, *viz.*, (1) natural dispersions of natural rubber, in particular the latex of *Hevea brasiliensis*; (2) artificially prepared dispersions of natural rubber; (3) dispersions of artificial or synthetic rubber in which the rubber-like material has been formed from pre-dispersed parent material; (4) artificially prepared dispersions of artificial or synthetic rubber. It is convenient to discuss these in substantially the reverse order to that in which they have just been enumerated.

Artificially prepared dispersions of synthetic rubber-like materials are latex-like fluids which can be applied in the same way as natural latex to manufacturing purposes and not only impart any advantageous features of the dispersed material, but also possess a potential advantage in that dispersing agents can be selected which are resistant to attack by, or to growth of, bacteria or moulds with consequent enhancement of stability, or which are favourable to the water-resistance of the final product.

Selection of the dispersing agent is also possible in the production of artificial dispersions of natural rubber, but in this case protein from the original latex is also normally present and retains its tendency to gradual chemical change under the influence of hydrolytic agents introduced, for example, with the preservative, or arising in the form of enzymes.

Of the synthetic rubbers which have attained commercial production in the last few years the best known are produced initially as dispersions or latices. "Neoprene" is obtained by the polymerisation of a stabilised aqueous dispersion of chloroprene  $\text{CH}_2:\text{CCl}.\text{CH}:\text{CH}_2$ . The electrically charged layer responsible for the stability of the parent dispersion persists in the resulting dispersion of the polymerised material. The forms of Buna synthetic rubbers distinguished by a letter, e.g., Buna N and Buna S, are also derived by the polymerisation of aqueous dispersions containing butadiene. In addition to the butadiene, the parent dispersion contains also a second polymerisable substance (acrylic nitrile and styrene respectively) and in each case co-polymerisation, or inter-polymerisation, occurs with formation of long molecules in which nuclei of both types are associated in chain-like formation. The properties of the resulting homogeneous products are distinct from those of products obtained by polymerisation of the parent substances singly and subsequent mixing of the polymerised dispersions. The nature of the adsorbed film influences the rate and result of the polymerisation process;<sup>1</sup> indeed the extensive patent literature includes numerous instructions as to the selection of appropriate stabilising or protective colloids for the primary dispersions.

In the foregoing types of dispersions of rubber-like material the electrical double layer is such that the globules normally exhibit the behaviour of negatively charged particles. Qualitatively, therefore, their electrophoretic behaviour is similar to that of natural *Hevea* latex, concerning which scientific investigation of the electrical double layer, and its related phenomena, is fuller.

Contrary to an almost natural assumption, the formation of rubber articles by electrodeposition of rubber from latex, as practised in the well-known "Anode" process, is not electrophoretic in character. The rubber deposit is formed essentially by the coagulation of the latex at the surface of a zinc anode (by zinc ions formed thereat by the current) or at the surface of a porous membrane surrounding the anode (by ions migrating from the anode space which contains an appropriate solution, e.g. of a calcium salt). An electro-osmotic effect, however, is observable in the tendency of the formed wet deposit, with continued passage of the current, to act as a capillary membrane and to lose water by electro-osmosis.

Quite recently the electrical behaviour of the rubber globule has been applied to the production of concentrated latex by a procedure parallel to that adopted by W. Pauli and his co-workers for the separation of hydrophilic colloids into layers of low and high concentration respectively, by carefully controlled electrodialysis or electrodecantation. In the process as applied to *Hevea* latex<sup>2</sup> the electrophoretic movement is caused not only to effect localised concentration of the latex but also, by occasional short reversals of the potential, to prevent permanent attachment of rubber particles to the membrane. The concentrated latex separates gravitationally to form an upper stratified layer which can be separated mechanically and continuously.

In natural *Hevea* latex it can be shown by careful observation of the electrophoretic migration of the rubber particles that the adsorbed film, with which the electrical double layer is associated, normally consists of

<sup>1</sup> I. Williams and H. W. Walker, *Ind. Eng. Chem.*, 1933, **25**, 199.

<sup>2</sup> B.P. 492,030.

protein.<sup>3</sup> Incidentally it may be remarked that the coagulation phenomena of *Hevea* latex generally are well known to show notable parallelism with the behaviour to be expected of a not very highly hydrated protein substance. The amphoteric nature of the rubber protein renders it possible, by reduction<sup>4</sup> of the *pH* to give the rubber particles in *Hevea* latex a positive electric charge instead of the original negative one. A similar effect can be obtained by addition of multivalent cations, *e.g.* of thorium<sup>5</sup> or by addition of a "cationic soap," *i.e.* a substance giving rise to a colloidal positive ion. With latex so treated, cathodic deposition can be effected whereas, normally, the electrodeposition of rubber is anodic. Although there are differences of opinion, such evidence as there is available indicates that the colloidal particle in rubber latex is relatively slightly hydrated.<sup>6</sup> Indeed, the difficulty which is experienced in the complete removal of the adsorbed protein by repeated dilution and concentration by removal of part of the aqueous phase, gives some indication of denaturation accompanying adsorption so that the latter process is not completely reversible.

Investigation of the nature of the electrophoretic behaviour of the rubber particle of preserved *Hevea* latex<sup>3</sup> has indicated that under special conditions of dilution and of *pH* the adsorbed film may not consist entirely of protein, and that the fatty acid soap in the latex may form part of the surface layer. Replacement of the protein layer by a film of other composition is possibly more definitely demonstrated by the alteration in the isoelectric point of the latex globules when certain other protective colloids are added.<sup>7</sup> In these circumstances the normal protein can become so effectively displaced that the dispersed particles show no sign of inversion of electric charge even at a *pH* value of 2, whereas normally the isoelectric point occurs at a value of approximately 4.5. Reference has already been made to the indications that the protein layer is probably in a partly denatured condition, so that the reversibility of its adsorption and complete displacement of the protein may be affected.

Recent investigations<sup>8</sup> have suggested that the protein of preserved *Hevea* latex is not a single substance, but comprises two proteins of distinct isoelectric value, *viz.* 4.5 and 3.9. It appears uncertain whether these values represent two different proteins in the original latex, or whether either corresponds with a partial degradation-product of the original protein.

Spontaneous coagulation of *Hevea* latex has been observed at much higher values of *pH* than the value normally associated with the coagulation phenomenon. This observation likewise may have an explanation in the hydrolysis of the adsorbed protein, *e.g.* by enzyme influences, with formation of amino acids such as arginine, which is known to be present in the hydrolysis products of rubber protein,<sup>9</sup> and which has an isoelectric point at *pH* approximately 10. It may be only a coincidence that guanidine, the nucleus of which is present in the arginine molecule, can itself act as a coagulant for latex under certain conditions.<sup>10</sup>

<sup>3</sup> I. Kemp and D. F. Twiss, *Trans. Faraday Soc.*, 1936, **32**, 890.

<sup>4</sup> B.P. 301,100; B.P. 334,581.

<sup>5</sup> B.P. 305,630.

<sup>6</sup> D. F. Twiss and A. S. Carpenter, *Proc. Rubber Technology Conf.*, 1938, 83.

<sup>7</sup> *E.g.*, see D. F. Twiss, *Trans. Inst. Rubber Ind.*, 1931, **6**, 426.

<sup>8</sup> C. Bondy and H. Freundlich, *Compt. rend. Lab. Carlsberg, Ser. Chim.*, 1937, **22**, 89.

<sup>9</sup> T. Midgley, A. L. Henne, and M. W. Renoll, *J. Amer. Chem. Soc.*, 1937, **59**, 2502.

<sup>10</sup> B.P. 377,751.

A set of observations with dialysed *Hevea* latex gives interesting additional information on the electrical behaviour of the rubber globule. If a series of portions of ammonia-preserved latex are subjected to graded alteration in  $pH$  it is found that coagulation occurs over a range from 5.75—2. If, on the other hand, the same latex has first been submitted to dialysis through a collodion membrane the range of coagulation is much less wide; so sharp indeed is the coagulation point ( $pH$  approximately 4.3) that unless the addition of the acetic acid is effected cautiously it is easy to over-shoot the isoelectric point, and to pass unintentionally to the condition of a stable positive latex. This result has a possible parallel in the observation that purification of *Hevea* latex "by centrifuge and/or by dialysis" facilitates the avoidance of coagulation when a "cationic soap" is added for reversal of the electric charge on the rubber particles.<sup>11</sup>

In our experiments the latex in each case was diluted to a dry rubber content of 12 per cent. and 10 c.c. portions of each were run into a series of glass tubes. To each set various quantities of diluted acetic acid were added followed by vigorous stirring. After two hours, the clots were removed, washed, sheeted, dried for twenty-four hours at 100° C. and weighed. The  $pH$  values of the sera were determined by means of the glass electrode.

The latex examined was derived from one lot of ammonia-preserved latex by the various treatments indicated below:—

(A) Normal ammonia-preserved latex.

(B) The latex which had been treated with formaldehyde to remove the ammonia.

(C) The latex which had been dialysed against distilled water for three days.

(D) Dialysed latex (C) to which had been added potassium sulphate to give a final concentration 0.1 N.

(E) Dialysed latex (C) to which had been added ammonium acetate to give a final concentration 0.1 N.

The results plotted in Figs. 2 and 3 show that both dialysis and treatment with formaldehyde have the effect of reducing the  $pH$  range over which coagulation takes place. The  $pH$  value at which maximum coagulation occurs is more definite with dialysed latex than with formaldehyde-treated latex, the difference being due, most probably, to the removal, by dialysis, of ions other than the ammonium ion.

The addition of a small quantity of ammonium acetate or potassium sulphate to the dialysed latex causes coagulation again to take place over a wide  $pH$  range (Figs. 4 and 5).

The greater range of  $pH$  over which coagulation occurs with normal ammonia-preserved latex than with the same latex after dialysis is,

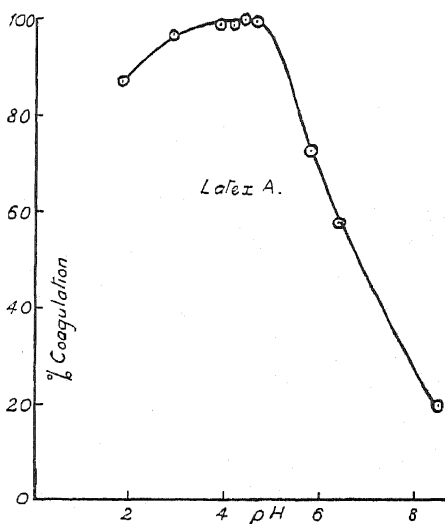
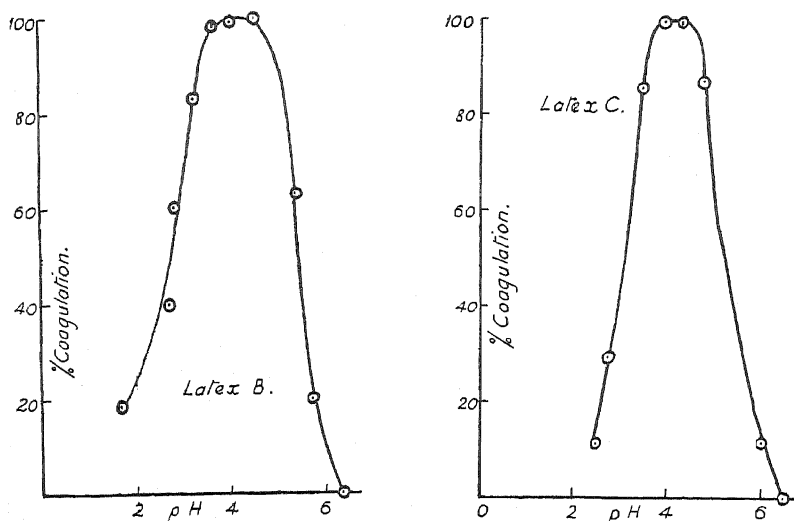


FIG. 1.

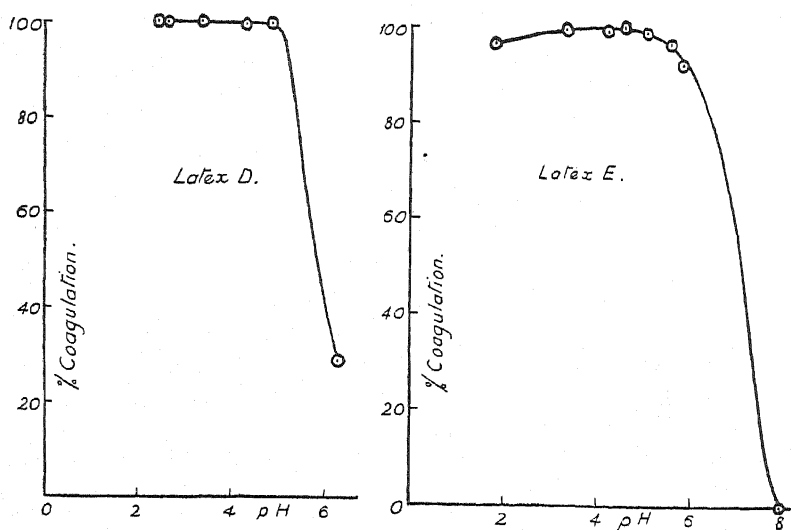
<sup>11</sup> C. M. Blow, *Proc. Rubber Tech. Conf.*, 1938, 190.

therefore, attributable to the presence of saline substances, derived from the ammonia and from the serum. This result is in accord with the



FIGS. 2-3.

knowledge that salts broaden the range of pH over which coagulation of a protein can take place and that in the absence of salts the coagulation pH of the protein is more critical.<sup>12</sup> The observed influence of dialysis



FIGS. 4-5.

on the coagulation behaviour consequently provides additional evidence of the existence of a protein layer on the rubber particles in *Hevea* latex.

<sup>12</sup> H. Chick and C. H. Martin, *Kolloidchem. Bei.*, 1913, 5, 49.

This effect of the natural saline constituents of the serum on the coagulation of latex by acetic acid may occur by way of combination of their ions with ionised groupings of the protein with the formation of undissociated groupings and consequent reduction in total charge on the protein. The effect may take place on both sides of the isoelectric  $pH$ , combination being between the positively charged protein molecule and the negatively charged ions from the saline substance in more acid media and between the negatively charged protein molecule and the positively charged ions from the saline substance in more alkaline media. The charge acquired by a protein molecule at  $pH$  values on either side of the isoelectric  $pH$  is therefore less, and the coagulation range greater, in the presence of soluble salts. It can be inferred from experiments which measure the combination of ions with gelatine<sup>13</sup> that this effect in the reduction of the charge is more marked on the alkaline side of the isoelectric  $pH$  than on the acid side. Adsorption phenomena between the charged protein and the appropriate ions of the saline substances present could also lead to this type of influence on the coagulation behaviour. The effect in either case would appear to be analogous in origin with the well-known coagulant effect of extraneous multivalent ions, *e.g.* of zinc (see p. 263) or aluminium.

The marked ability of some colloidal substances, *e.g.* sodium alginate, gum tragacanth, etc.<sup>14</sup> to accelerate the creaming of *Hevea* latex, and its dependence in some cases on the presence of an additional colloidal substance without creaming activity, are other effects which are probably related with the activity of an adsorption layer at the surface of the dispersed rubber particles.

As has already been mentioned the constituent of normal latex, which is mainly responsible for the formation of the protective layer on the dispersed rubber particles, is of protein character. In the preparation of the ordinary forms of rubber, such as pale crêpe rubber or smoked sheet, the protein remains associated with the rubber and constitutes approximately 2 or 3 per cent. of the dry material where its presence causes impairment of the water-resistance of the rubber hydrocarbon. Effective displacement of the protein layer (and exclusion of surplus protein dissolved in the serum) by other adsorbed layers of less hydrophilic material, for the production of natural rubber with high resistance to water absorption, therefore, still constitutes a problem. Complete solution of this problem appears to be hindered by partial denaturation undergone by the adsorbed protein layer. The most effective procedure hitherto has been by a creaming process repeated several times, possibly combined with a process of creaming by centrifugation.

It is a well-known fact in rubber technology that the physical and mechanical properties of rubber, such as tensile strength and resistance to abrasion, to tearing and to solvents, can be profoundly modified by the incorporation of certain finely divided substances in the rubber. The actual mechanism by which this so-called "reinforcing effect" is produced is a problem which still awaits complete elucidation. It has generally been accepted that a reinforcing agent exerts a greater effect the more intimate its degree of dispersion in the rubber and that the interfacial energy and the intensity of wetting in the dispersed system are important factors, with which must be associated, in the most important case of carbon black, the adsorbent power of the incorporated

<sup>13</sup> J. H. Northrop and M. Kunitz, *J. Gen. Physiol.*, 1924, 7, 25.

<sup>14</sup> D. F. Twiss and A. S. Carpenter, *Proc. Rubber Tech. Conf.*, 1938, 81.



particles. The full reinforcing effect however is not immediately developed; a mixture of masticated rubber and carbon black (containing for example 20 per cent. of the latter) may be completely soluble in ordinary rubber solvents initially but on storage for a few days it becomes tough, resistant to tearing and insoluble.<sup>15</sup> Recently indications have been obtained that the reinforcing effect is enhanced if a rubber—carbon black mixture, prior to vulcanisation, is subjected to a heat treatment,<sup>16</sup> e.g. at 132° (and remilling), and that this alteration in the effect arises from some form of flocculation of the dispersed particles of carbon black in the temporarily softened rubber. The result may be likened to the formation of a gel from an aqueous dispersion of a colloidal clay. The desirable flocculation which is believed to underlie the increase in reinforcing effect can also occur during the heating period necessary for vulcanisation,<sup>17</sup> and so is favoured by retardation of the vulcanisation process by means other than the lowering of the temperature. A favourable influence can also be exerted by the presence of small proportions of certain substances such as cetyl pyridinium bromide and lauryl pyridinium sulphate, which in spite of an accelerating effect on vulcanisation appear to assist the flocculation process.

The probable importance of the adsorptive action of carbon black in these reinforcement phenomena is emphasised by the observation that previous removal of the natural fatty acid constituents of rubber (by acetone extraction) renders the satisfactory dispersion of carbon black in the rubber, by milling, more difficult, but that incorporation of stearic acid restores the facility of dispersion.<sup>18</sup> Indeed a tentative calculation has indicated that the maximum proportion of carbon black which can be effectively dispersed in rubber corresponds approximately with the quantity for which the natural fatty acids of the rubber suffice to form a unimolecular surface layer.<sup>19</sup>

Possibly some light is thrown on this phenomenon by an investigation of the behaviour of dispersions of carbon black particles in organic media other than rubber.

Although it is possible to make an apparently stable dispersion of carbon black in rubber by the customary drastic milling or mixing operation, the apparent stability of the resulting dispersion probably arises largely from the viscous character of the medium. Such a mechanically prepared mixture of rubber and carbon black (with a low proportion of the latter) can also be dissolved in benzene to give a dispersion of considerable degree of permanence which is probably attributable again to the same cause. On the other hand it has not been found possible to produce a permanent dispersion of carbon black in benzene or in a solution of rubber in benzene by prolonged grinding (e.g. in a pebble mill) without any additional colloid material, flocculation occurring spontaneously, almost at once in the former case and more slowly in the latter.

It appears probable therefore that mechanically prepared dispersions of carbon black in rubber are inherently unstable and that although flocculation may be so slow as to be inappreciable at ordinary temperatures,

<sup>15</sup> P. Stamberger, *Colloid Chemistry of Rubber*, Oxford University Press, 1929, pp. 54, 57; *Kautschuk*, 1931, 7, 182.

<sup>16</sup> B.P. 493,552; U.S.P. 2,118,601; C. R. Park and P. P. McClellan, *Ind. Eng. Chem.*, 1938, 30, 704.

<sup>17</sup> E. A. Grenquist, *ibid.*, 1928, 20, 1073.

<sup>18</sup> C. R. Park and V. N. Morris, *ibid.*, 1935, 27, 582.

<sup>19</sup> J. T. Blake, *ibid.*, 1928, 20, 1084.

flocculation will always set in when the conditions of temperature, and consequently reduced viscosity of the medium, permit the necessary movement of the particles. With aniline (dielectric constant 7.3, dipole moment  $1.56 \times 10^{-18}$  e.s.u.) as dispersion medium it is possible in a pebble mill to produce a semi-stable dispersion of carbon black, flocculation of which is observed only after several days while with nitrobenzene (dielectric constant 34, dipole moment  $3.9 \times 10^{-18}$  e.s.u.) the resulting dispersion is stable. It seems reasonable therefore to assume that the dielectric constant of carbon black is so near that of benzene (2.3) and of rubber (2.2) that the electric charges resulting from the contact of the particles with these media are too small for the dispersions to show permanent stability. Orientation of the polar molecules around the charged particles may lead to a further increase in the stability of the dispersions in nitrobenzene or aniline. Cetyl pyridinium bromide also causes the flocculation of an otherwise stable dispersion of carbon black in nitrobenzene. The unstable dispersion of carbon black in benzene is not observably affected by cetyl pyridinium bromide.

It can be shown that in an electric field carbon black particles dispersed in benzene or nitrobenzene tend to move anode-wards, but the main effect is a formation of continuous strings of particles reaching out from the electrodes particularly from the anode; oscillation of isolated particles from electrode to electrode may also be observed especially in benzene. These results of ours appear to be comparable with the well-known Lodge-Cottrell effect, and are probably explained by the high electrical conductivity of the dispersed material and the low conductivity of the dispersion medium. They are also in accord with an earlier observation that carbon black contains isotropic and anisotropic particles.<sup>20</sup> With cetyl pyridinium bromide present the results are somewhat different, the movement of the particles indicating a swirling of the liquid while the stringing of the particles is less pronounced. Dispersions of carbon black in rubber itself also give evidence of such stringing of the particles. Application of a pulsating electric potential induces rapid increase in the electrical conductivity of the dispersion (*i.e.* of the compounded rubber) and the effect is accentuated by the presence of cetyl pyridinium bromide and similar substances.

We have to express our indebtedness to the Dunlop Rubber Co. in the Chemical Research Department of which the new experiments here incidentally recorded were made.

*Dunlop Rubber Co., Ltd.,  
Birmingham.*

<sup>20</sup> E. A. Grenquist, *Ind. Eng. Chem.*, 1929, **21**, 665.

# THE ANODIC DEPOSITION OF OLEO-RESINOUS LACQUERS.

By C. G. SUMNER.

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In the canning industry, certain types of pack require cans which are internally lacquered, in order to prevent undesirable interactions between the metal surface and the foodstuff. The usual method of making lacquered cans is to form them from tinplate which has been lacquered in flat sheets, but it is impossible to obtain an absolutely continuous coating over the interior of a formed can by this means. For foodstuffs of a neutral character the degree of imperfection is not serious, but in the case of acid packs such as fruits, corrosion of the metal proceeds at discontinuities in the lacquer coating. It has for many years been urged that at least one coat of lacquer should be applied after forming the can,<sup>1</sup> and various methods are now being developed for this purpose.

One means of solving this problem has been advanced by W. Clayton,<sup>2</sup> who suggested the application of lacquer by electrodeposition from an emulsion. The anodic deposition of dispersed materials such as japan,<sup>3</sup> synthetic resins,<sup>4</sup> and rubber,<sup>5</sup> was already known, but this conception was an innovation in can-making technology. The present writer has been largely responsible for developing the Clayton process on an experimental basis, and while it has not yet reached commercial application, the outstanding practical problems are of an economic and engineering character, the method being extremely successful from a laboratory point of view.

## Essential Features.

The lacquers used for ordinary food cans are of the oleo-resinous type, and normally possess sufficient free acidity to emulsify readily in an alkaline solution. In the early experiments, dilute ammonia was used as the emulsifying medium. The lacquer globules are negatively charged, and deposition is therefore effected at the anode, as in various similar processes. The deposit usually has considerable resistance, so that the current rapidly falls, but it remains conductive and the thickness may be built up by prolonging the treatment. Quite thin deposits are aimed at; the weight of a typical stoved lacquer film is about 5 mg. per sq. in., and the time required for deposition is a few seconds only, so that the application of the process to a mass production line is feasible.

For the best results, it has been found desirable to submit the cans to a preliminary degreasing process, and for tinplate an electrolytic method has been developed by the writer,<sup>6</sup> which gives effective cleaning in a few seconds and so enables the various operations to be kept in step.

<sup>1</sup> Morris and Bryan, *D.S.I.R. Food Investigation Board Special Report*, No. 40, 1931, p. 5.

<sup>2</sup> Clayton, Sumner, Morse and Johnson, B.P. 455,810, 1936.

<sup>3</sup> Davey, U.S.P. 1,294,627, 1919.

<sup>4</sup> Davies, B.P. 291,477, 1928.

<sup>5</sup> Sheppard and Eberlin, U.S.P. 1,476,374, 1923. Klein, B.P. 223,189, 1924.

<sup>6</sup> Sumner, B.P. 479,681, 1938.

Deposition is effected by inserting a cathode into the can, filling the intervening space with emulsion and passing current. After deposition, the film is washed free of emulsion, using soft or distilled water in order to avoid coagulating the emulsion, and it is then seen as a milky coating which contains an aqueous phase as well as lacquer. The milkiness disappears as the water is lost by evaporation and the lacquer particles coalesce, and when stoved as usual the coating has the normal appearance of a lacquer film. The presence of soldered seams in the can imposes a limitation on the permissible stoving temperature.

An important advantage of using the lacquer in emulsion form is that the viscosity of the disperse phase may be kept high while that of the emulsion as a whole is low. This makes possible an economy in volatile thinners, which are normally added to a lacquer intended for mechanical application in order to reduce the viscosity to a suitable value.

The early experiments were mainly concerned with the practical factors involved in obtaining films which were satisfactory in respect of continuity and weight per unit area, but attention was directed later to more fundamental aspects of the process. Owing to the almost infinite variety of possible lacquer compositions, a considerable amount of work would be necessary in order to establish general theoretical relationships, and the results so far obtained are largely empirical, but they do open up some interesting problems and speculations.

### Mechanism of Deposition.

The usual account of the electrodeposition of rubber<sup>7</sup> is that the negatively charged rubber particles are coagulated by positive ions (*e.g.*, zinc ions in the case of a zinc anode), migrating away from the anode. That a similar indirect mechanism operates here is shown by various facts, which will receive more detailed attention later.

(1) The current-time curve is in general of sigmoid form, with an initial period during which no deposition occurs and the current remains fairly steady, followed by a rapid and then a progressively more gradual fall in the current as deposition sets in.

(2) The weight of lacquer deposited per coulomb is not invariable, but for a given lacquer depends on such factors as emulsion composition and applied voltage.

A somewhat different picture of the mechanism has proved useful, however. The lacquer emulsion is stabilised by soap-like compounds which are formed by interaction of the alkaline medium with acidic constituents or groupings in the lacquer, so that the particles will become negatively charged as a result of ionisation. The medium does not contain anions which will cause tin to pass into solution as cations, and the primary anode reaction will be hydroxyl ion discharge. Removal of hydroxyl ions (balanced electrically by the migration of alkali metal ions away from the anode) will tend to lower the *pH* value in the vicinity of the anode, but in opposition to this tendency there will be a buffer action due to the emulsifying agent, which is the salt of a weak acid. This buffer action may be represented as follows:



where HA is the unionised acid, A' the anion, and the square brackets refer to a lacquer particle. The negative charge on the particle is therefore reduced as a consequence of the buffer action called into play by the primary electrode reaction, and if it is made small enough, coagulation of the particles will occur.

<sup>7</sup> Beal, *Ind. Eng. Chem.*, 1933, 25, 609.

Hydroxyl ion discharge at the anode results in an oxidation of the tin surface, which has the practical effect of preventing discoloration of the tin by sulphur bearing foodstuffs.<sup>2, 6</sup> The occurrence of anodic oxidation has been confirmed by determining the current-time curves, under given electrical conditions, for tinplate in (a) a lacquer emulsion, (b) an alkaline electrolyte. In both cases, where the original surface film of oxide, etc., on the tinplate had been removed by a preliminary electrolytic treatment, there was at first a slow decline in current (to a limiting value in the case of (b)); if the preliminary treatment had consisted of "defilming" followed by anodic oxidation, the current remained steady (until the onset of lacquer deposition, in the case of the emulsion), the limiting value being attained immediately.

### Emulsions in Sodium Aluminate Solution.

The conception of the deposition as due to local hydrolysis suggested that a similar effect might be obtainable in a simple electrolyte, such that hydrolysis of the anion would yield an insoluble compound. An electrolyte of this kind is sodium aluminate, and it was found in fact possible to coat tinplate with alumina (or hydrated alumina) by anodic treatment in sodium aluminate solution.<sup>8</sup> The deposit was porous, and therefore conductive when wet, and lacquer could be electro-deposited on top of it from an ammoniacal emulsion. A considerable improvement in the uniformity and continuity of the lacquer film was effected in this way.

A further idea was the idea of depositing alumina and lacquer simultaneously, and this was achieved by emulsifying the lacquer directly in sodium aluminate solution.<sup>8</sup> This procedure involves the decomposition of a certain proportion of the aluminate by the lacquer acids, but within certain limits (depending on the lacquer) this does not cause destabilisation of the emulsion. It was thought at first that only lacquers of low acidity would form stable emulsions in this medium, but systematic experiments<sup>8</sup> have shown actually that the character rather than the proportion of the acidic constituents is the important factor, and a high acidity (measured by the "acid value") is beneficial if the sodium salts formed are good emulsifying agents. A copal lacquer having an acid value of about 30 gave a stable emulsion in its own weight of 1 per cent. sodium aluminate solution, for example. There is an upper limit to the permissible aluminate concentration, depending on the lacquer; many lacquers have been found to emulsify satisfactorily in 1 per cent. solution, but one example showed coagulation at this concentration, whereas it was stable in 0.5 per cent. aluminate. This is possibly a salting-out effect.

The characteristics of the emulsion, both in respect of stability and of the type of deposit obtained, depend on (1) the acid value of the lacquer, (2) the strength of the acid constituents, (3) the concentration of sodium aluminate in the emulsion, (4) the phase ratio of the emulsion. Ultimately these factors reduce to the concentration or activity ratio of aluminate ions to "emulsifier" ions in the final emulsion, and the relation between their hydrolysis constants. These will determine the ratio in which the two types of ion contribute to the buffer action at the anode, and therefore the ratio of alumina to lacquer in the deposit. By adjustment of the emulsion composition, differences in lacquer

<sup>8</sup> Sumner, Johnson and Clayton, B.P. 492,900, 1938.

characteristics may be compensated so as to obtain the desired type of coating.

Part of the alumina (or other aluminium compound) in the deposit may arise from the deposition of alumina precipitated during emulsification, but that hydrolysis of aluminate ions plays an important part is shown by various facts.

(1) Increase in the phase ratio (lacquer to solution) will increase the amount of precipitated alumina, in direct proportion to the emulsifying agent formed, but it will reduce the concentration of aluminate ions. In practice, an increase in the phase ratio *diminishes* the proportion of alumina in the deposit.

(2) Addition of free alkali to the aluminate solution results in an *increase* in the proportion of alumina in the deposit. Alkali metal tartrate, which tends to prevent the precipitation of alumina, acts similarly.

### Quantitative Relations : Structure of the Deposit.

The amount of lacquer deposited in a given time, with given initial electrical conditions, depends on (i) the weight deposited per coulomb, and (ii) the quantity of electricity passed in the given time. The first factor is some function of the emulsion stability, *i.e.*, of the double layer potential, while the second depends on the rate of decrease of the current with time; this in turn involves the rate of deposition, and also the closeness of packing of the coagulated particles, which determines the rate of increase of the film resistance with the weight of material deposited.

Quantitative experiments on this process have therefore been based on determinations of the current/time curves, coupled with film weight measurements. A parallel-sided cell is used, one side being formed by the sheet of tinplate which is to be coated, clamped against a gasket. For accurate plotting of the current/time curve a 9.5 mm. cine-camera has been employed, the ammeter, voltmeter and stopwatch being photographed simultaneously at the rate of 8 frames per second; after development the film is examined under low magnification and the readings plotted. The quantity of electricity passed in any experiment is obtained by graphical integration of the area under the curve.

This method is tedious, and in later experiments visual observation of the ammeter has been used, in conjunction with a variable automatic time-switch and a form of water coulometer adapted to measure quantities up to 5 coulombs. For each set of conditions a series of different deposition periods is used (usually 2, 4, 6, 8 and 10 seconds), the initial and final values of the current being recorded in each case. The weight of the film (after stoving under standard conditions) is also determined for each experiment

Let  $E$  = total applied E.M.F.,  
 $\eta_0$  = initial back E.M.F. (due to polarisation),  
 $\eta$  = back E.M.F. after time  $t$ ,  
 $r_0$  = initial resistance of dispersion,  
 $r_t$  = resistance due to deposit, after time  $t$ ,  
 $R$  = external (series) resistance,  
 $I_0$  = initial current,  
 $I$  = current after time  $t$ .

Applying Ohm's Law to the circuit as a whole, we have for the initial state and time  $t$ , respectively,

$$(E - \eta_0) = (R + r_0)I_0 \quad (1)$$

$$(E - \eta) = (R + r_0)I + r_f I \quad (2)$$

whence  $(\eta - \eta_0) = (R + r_0)(I_0 - I) - r_f I,$

or  $r_f I + (\eta - \eta_0) = (R + r_0)(I_0 - I). \quad (3)$

If the fact that  $(\eta - \eta_0)$  includes a relatively small change in the cathode polarisation is neglected, the left-hand side of this equation, which may be written  $V_f$ , represents the additional P.D. which must be overcome owing to the presence of the film. The plot of  $V_f$  against film weight forms a convenient criterion for the effect of various factors on the deposition process; alternatively the ratio

$$V_f/Ir_0 = (R/r_0 + 1)(I_0/I - 1)$$

may be used.

For consideration of the structure of the deposit, however, the variation of  $r_f$  with film weight is required, and this is not obtainable

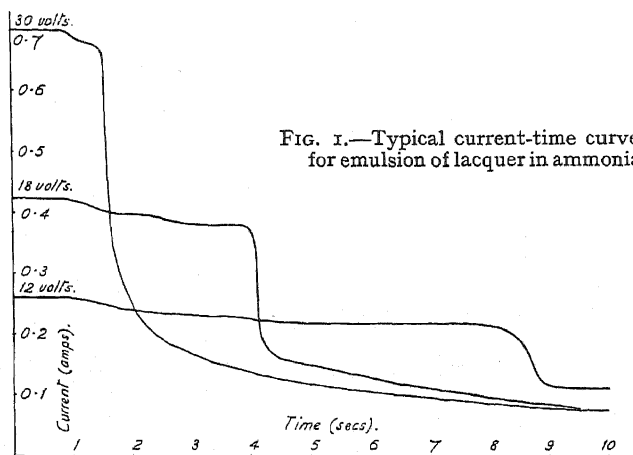


FIG. 1.—Typical current-time curves for emulsion of lacquer in ammonia.

directly from (3), since  $(\eta - \eta_0)$  is not known. During deposition of the film, the actual current density will almost certainly increase, although the total current diminishes, since metal is then exposed only at the pores. Hence  $(\eta - \eta_0)$  may become quite large; once the surface is covered, however, the further variation in  $\eta$  will be relatively slight, and over the range where the film is thickening it is probably legitimate to take  $\eta$  as approximately constant. We then have from (2),

$$\log (R + r_0 + r_f) = \log I/I + \text{constant},$$

whence  $d \log (R + r_0 + r_f) = -d \log I. \quad (4)$

Hence if  $(R + r_0)$  is kept constant, the slope of the  $\log (I/I)$ , film weight curve will give a measure of the rate of change of film resistance with film weight, under different conditions.

In Fig. 1 are shown the current/time curves for an emulsion of a typical lacquer in 1 per cent. aqueous ammonia, using a constant value of  $(R + r_0)$  but different applied voltages (12, 18 and 30 volts respec-

tively). In Fig. 2 are shown the corresponding film weight/coulomb curves. The following points emerge from a study of these curves.

(1) There is an initial period during which no appreciable quantity of lacquer is deposited; this evidently represents the period during which the emulsion is brought to the verge of instability at the anode surface.

(2) The quantity of electricity passed before deposition sets in decreases as the applied E.M.F. (and therefore the initial current) is increased. This is understandable since de-stabilisation is the nett result of the electrode process in modifying the ionic environment and of diffusion in tending to restore the original condition; the effect of diffusion will be relatively less at higher current densities.

(3) An appreciable amount of lacquer is deposited before the current diminishes, the major fall of current occurring abruptly over a small range of film weight. This may be due to a sudden change in the closeness of packing beyond a certain point, or it may happen that before the drop in current the de-stabilised particles are not adherent to the surface, but become so when the anode is rinsed.

(4) The weight/coulomb curves are linear, but the slope increases with the applied E.M.F.

If the data from these curves are plotted in the manner of equation (4), (*i.e.*,  $\log 1/I$  against film weight), it is found that over the weight range where the 18-volt and 30-volt experiments overlap, the two curves are practically identical in form though displaced in position. This means that for a given film weight, the structure of the film is independent of the E.M.F. On the other hand, the efficiency of deposition increases with the E.M.F. The latter effect has been confirmed for many diverse emulsions; it holds not merely when  $(R + r_0)$  is kept constant but also when  $I_0$  is kept constant, for different values of  $E$ . No wholly satisfying explanation has yet been found, but it may be due to the fact that the higher the E.M.F., the more slowly will the current decline with increase in film weight, *e.g.*, for a given  $I_0$  and given film weight the final value of  $I$  will be higher. This means that the deposition will occur more rapidly, and at a higher average current density, so that the relative effect of diffusion will be less and the local diminution in  $pH$  greater, with correspondingly more effective coagulation. Nevertheless, the constancy of the slope of the weight/coulomb curve under conditions of diminishing current remains surprising; this effect also has been found with many different emulsions.

Systems including sodium aluminate are more complicated from a quantitative aspect than the example detailed above. An increase in the ratio of aluminate to lacquer gives a more rapid rise in  $V_f$  with film weight, indicating that the co-deposition of alumina tends to clog the pores or to form a more compact deposit. At the same time the

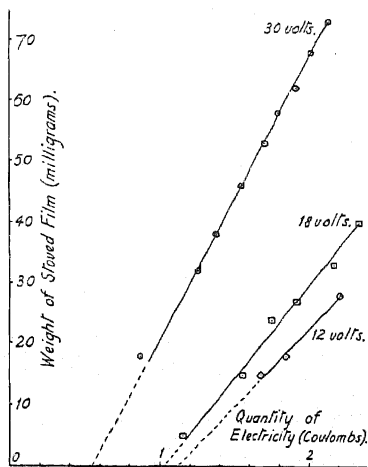


FIG. 2.—Weight-coulomb relations corresponding with Fig. 1.



slope of the weight/coulomb curve is diminished, as is to be expected since the "electrochemical equivalent" of an aluminate ion is much less than that of a lacquer particle. Deposition sets in almost immediately, and the weight of material deposited before the current falls is small.

### Conclusion.

Although the electrical double layer as such has hardly been mentioned in the above discussion, it is evident that the detailed mechanism of the process must present many features identical with the ordinary coagulation of colloids. The chief difference is that coagulation occurs as a secondary effect of the anodic reaction, without the introduction of extraneous ions into the system but with local differences in ionic environment.

In conclusion, I acknowledge with pleasure the valuable contributions of a number of colleagues to the development of this process: Dr. W. Clayton, who originated the work; Mr. F. D. Farrow (Director of Research, The Metal Box Company, Ltd.), under whom it has been continued; J. F. Morse and R. Waite, who carried out some of the physico-chemical experiments; R. I. Johnson and P. Renold, who collaborated in the engineering aspects. Finally, I am indebted to the Metal Box Company, Ltd., who hold all patent rights in the process, for permission to publish this paper.

### Summary.

A method of lacquering metal surfaces by electrodeposition, developed primarily for the internal coating of tinplate cans after fabrication, is outlined. When current is passed through an emulsion of an oleo-resinous lacquer in an alkaline medium, a deposit is produced by the coagulation of negatively charged lacquer particles as a result of changes in the ionic environment at the anode. By emulsifying the lacquer in sodium aluminate solution, coatings containing arbitrarily variable proportions of lacquer and alumina (or other aluminium compound) may be obtained. The significance of the current/time and film weight/coulomb curves is discussed in relation to the mechanism of the process and the structure of the deposit. The film weight has been found in general to bear a linear relation to the quantity of electricity passed, but the slope increases with the applied E.M.F., even when the initial current density is given.

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# FORMATION OF A DEPOSIT BY ELECTROPHORESIS.

BY H. C. HAMAKER.

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## 1. Introduction.

In the delicate experiments designed to measure the electrophoretic velocity of colloidal particles, it will hardly ever be realised whether the particles are merely concentrated at one of the electrodes, or actually deposited on it. Hence little attention has hitherto been paid to the formation of a deposit by electrophoresis. As a technical application the electro-deposition of rubber from latex<sup>1</sup> has been long known. Moreover, Patai and Tomaschek<sup>2</sup> have described a method for preparing colloidal solutions of barium and strontium carbonate in water or in alcohols from which electro-deposition is easily effected. These are the main papers dealing with the subject.

In the experiments described below, we have used a different technique, originally suggested by Dr. J. H. de Boer, which is applicable to an almost unlimited variety of substances. A brief account of this method has already been published elsewhere.<sup>3</sup>

The essential point is that we used suspensions in an organic medium, such as alcohols, acetone, etc., prepared in a very simple way by grinding the powdered material with the dispersion fluid in a ball mill. Sometimes grinding was not even necessary, satisfactory suspensions being obtained simply by shaking the powder with the fluid. From such suspensions an electrophoretic coating can be applied in a few seconds only, especially since the concentration can be very high and voltages of 100 v. and more can be used.

Some conditions essential for the success of this method have been discussed in the paper read before the section on colloid stability.<sup>4</sup> In the present paper we will describe some experiments made with suspensions of  $\text{BaCO}_3$ ,  $\text{BaSr}(\text{CO}_3)_2$ , a mixed crystal 1:1 of  $\text{BaCO}_3$  and  $\text{SrCO}_3$ ,  $\text{MgO}$ ,  $\text{MgCO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaF}_2$  in methanol, ethanol, acetone or mixtures of these fluids.

## 2. The Yield.

The "coating electrode"  $K^*$  is immersed centrally within a second electrode A (Fig. 1), 25 mm. in diameter and 35 mm. high. Since a moder-

<sup>1</sup> P. H. Prausnitz and J. Reitschötter, *Elektroforese, Elektrosiose, Elektrodialyse in Flüssigkeiten*, 1931.

<sup>2</sup> E. Patai and Z. Tomaschek, *Koll. Z.*, 1936, **74**, 253; 1936, **75**, 80.

<sup>3</sup> J. H. de Boer, H. C. Hamaker and E. J. W. Verwey, *Rec. trav. chim.*, 1939, **58**, 662.

<sup>4</sup> *This volume*, p. 180.

\* Since suspensions with both positive and negative particle charges occur it will be convenient to have a separate term to denote the electrode on which a deposit is formed regardless of the sign of its potential. As such we shall here use the term "coating electrode."

ate stirring does not as a rule hinder the formation of a deposit on K the stirrer R was used to prevent sedimentation during the experiments. The length of the coating electrode K was always 30 mm.

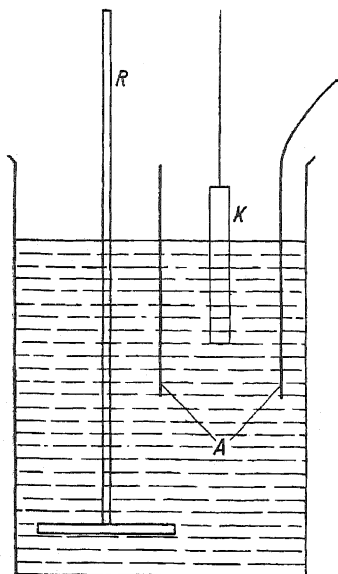


FIG. 1.—Experimental arrangement.

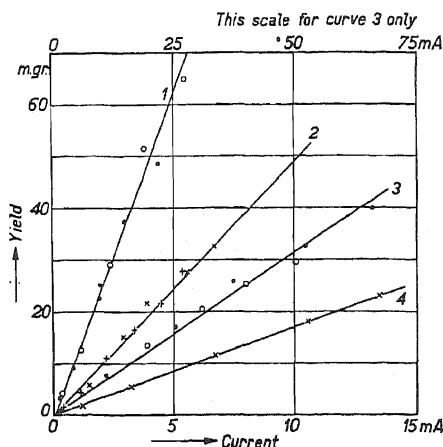


FIG. 2.—The yield as a function of the current, when the time is constant.

TABLE I.—EXPLANATION OF FIGS. 2, 3 AND 4.\*

Curve.	Substance.	Suspended in.	Concentration (gr./c.c.).	Volts.	Time (sec.).	Current (mA).	Diameter of Electrode (mm.).
1	BaCO <sub>3</sub>	M	6.2	20-200	3	0.3-5.2	0.1
2	BaSr(CO <sub>3</sub> ) <sub>2</sub>	EA	1.8	20-250	5	0.5-6.7	0.2
3	MgO	M	3.2	20-250	3	3-66	> 1
4	MgCO <sub>3</sub>	M	0.9	20-200	10	1.3-13	> 2
5	CaF <sub>2</sub>	E	12	100	0-10	decr.	0.1
				50	0-20	"	0.2
				20	0-40	"	1
6	BaSr(CO <sub>3</sub> ) <sub>2</sub>	EA	4.5	50	0.15	2.6	1
7	Al <sub>2</sub> O <sub>3</sub>	M	7.3	45	0-20	decr.	2
8	CaF <sub>2</sub>	E	5.7	50	0-30	"	0.4
9	BaSr(CO <sub>3</sub> ) <sub>2</sub>	EA	2.25	20	0-20	0.5	0.4
							1

\* In column 3 M means Methanol, E Ethanol and EA a mixture of Ethanol and Acetone 1 : 1. Decr. in column 7 signifies that the current decreases during electrophoretic deposition as shown in Fig. 4. The scale on top of Fig. 2 holds for curve 3 only.

The potential applied varied from 5 to 250 v.; computing the electric field at K for a voltage of 50 v. from the appropriate electrodynamic equations we obtain :—

Diameter of K. . . . .	0.5	1.0	2.0 mm.
Electric field at K . . . .	512	310	198 v./cm.

These data illustrate the conditions under which electro-deposition was observed.

The amount of material deposited which will be designated as the "yield" of an experiment is found by weighing K before and after applying a coating. When the voltage and the concentrations lie within certain limits (see § 3) the yield is proportional with the quantity of electricity which has passed. This is amply demonstrated in Figs. 2 and 3.

Complete data concerning the experiments to which these figs. refer are given in Table I. Fig. 2 represents cases where the time was constant and the voltage was varied, whereas curves 6 and 9 in Fig. 3 correspond to experiments where the voltage (and the current) were kept constant and the time was changed. For some suspensions the current rapidly decreases when electro-deposition is going on, as shown in Fig. 4; for such cases,  $\int_0^t I \cdot dt$  was computed from the  $i/t$  curves and the yield was plotted against the value of this integral (curves 5, 7 and 8 in Fig. 3). Again, straight lines through the origin were the result.

The decrease of the current depicted in Fig. 4 was originally attributed to a high resistance of the layer on the coating electrode. A simple computation proved that this resistance must have been from 5 to 20 times as high as that of the suspension. Now the layers deposited are rather porous (only 30 to 60 % solid material) and such a high resistance cannot readily be explained.

Besides, a  $\text{BaSr}(\text{CO}_3)_2$  suspension with which the current was originally perfectly constant showed a very marked decrease in the current after the addition of small amounts of certain electrolytes

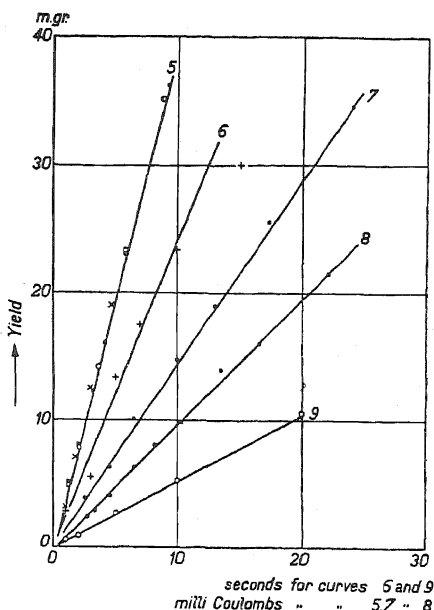


FIG. 3.—The yield as a function of the time (curves 6 and 9) or of the coulombs (curves 5, 7 and 8).

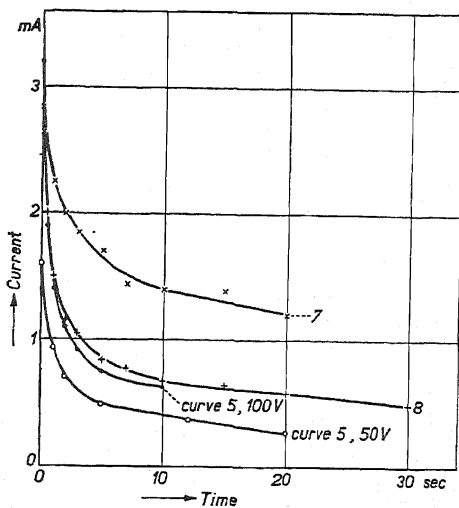


FIG. 4.—Decrease in the current during electro-deposition.

(for instance,  $\text{Na}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{MgSO}_4$ ). These observations suggest that the fall in the current must be explained by a strong polarisation in the coating rather than by a high resistance. Anyhow, the decrease in the current must be connected with a marked potential drop  $\Delta V$  across the coating. From the specific conductivity of the suspension, the current, and the diameter of the electrode + layer, the value of the potential difference in the suspension can be computed and the potential drop  $\Delta V$  across the layer is found by subtracting this value from the total voltage applied. Such calculations proved that  $\Delta V$  is roughly proportional to the current and the thickness of the layer, a result which is computible with both a high resistance of the layer and polarisation. In this way a decision could not be made. For layers of  $100\mu$  the potential drop  $\Delta V$  would occasionally amount to 70 or 80 % of the voltage applied.

By comparing the electric conductivity of the suspension with that of the clear fluid obtained by centrifuging it was ascertained that the conduction is almost entirely electrolytic. The contribution of the particles was, in our cases at least, negligibly small.

The proportionality of the yield with the coulombs demonstrated above is therefore, in itself, of little interest. We should preferably investigate the dependence of the yield on the strength of the electric field. However, when a strong polarisation occurs, as in the cases of Fig. 4, the voltage applied is not in the least a measure of the electric field prevailing in the fluid, whereas, assuming the conductivity of the suspension to be constant during an experiment, the current will be proportional to the field times the surface which is being coated.

$$\text{That is} \quad Q = \int I \cdot dt = \tau \iint dV/dn \cdot dS \cdot dt \quad . \quad . \quad . \quad (1)$$

where  $\tau$  designates the specific conductivity and  $dV/dn$  is the electric field perpendicular to the surface  $S$ .

By diluting suspensions with their filtrates we ascertained, moreover, that, *ceteris paribus*, the yield is (within certain limits, see § 3) proportional to the concentration.

Hence, combining these various results the yield is found to follow an extremely simple and straightforward law, being proportional to the time, the concentration, the surface which is being coated, and the electric field. This is expressed by

$$Y = \sigma \cdot c \cdot \iint dV/dn \cdot dS \cdot dt \quad . \quad . \quad . \quad (2)$$

$c$  denoting the concentration and  $\sigma$  a constant which will depend on the chemical composition of the suspensions but not on the physical conditions of the experiments. In our opinion, equation (2) embodies the correct interpretation of our observations.

### 3. Deviations from the Normal Law.

If in equation (2) we express  $c$  in  $\text{g.cm.}^{-3}$ ,  $dV/dn$  in  $\text{v. cm.}^{-1}$ ,  $S$  in  $\text{cm.}^2$  and  $t$  in seconds the constant  $\sigma$  has the dimensions  $\text{cm. sec.}^{-1}/\text{v. cm.}^{-1}$  and represents a lower limit for the electrophoretic velocity of the particles;  $\sigma$  will be equal to the electrophoretic velocity when every particle reaching the coating electrode actually partakes in the formation of a deposit, but if only a fraction of the particles is deposited,  $\sigma$  will be less.

If we wish to compare observations made under widely varying conditions, it is most convenient to calculate  $\sigma$  from every single observation. As long as equation (2) holds  $\sigma$  will be constant and deviations from (2) will be revealed by changes in the  $\sigma$  computed. By combining equations (1) and (2) we find

$$Y = \frac{\sigma \cdot c \cdot Q}{\tau} \quad \text{or} \quad \sigma = \frac{Y \cdot \tau}{c \cdot Q} \quad . \quad . \quad . \quad (3)$$

and this equation has generally been used for the computation of  $\sigma$  from such data as represented in Figs. 2 and 3; the specific conductivity  $\tau$  was determined from separate observations.

In Fig. 5  $\sigma$  has been plotted against the voltage applied. We see that above 20 v.  $\sigma$  is fairly constant, but at lower voltages  $\sigma$  rapidly decreases, showing that the electro-deposition of the suspended material becomes much less effective. Hence in practical applications the possibility of using high voltages is of very great importance.

Likewise, Fig. 6 represents  $\sigma$  against the concentration. Though  $\sigma$  is practically constant at high concentrations it will be noted that in some cases  $\sigma$  rapidly diminishes when the concentration is too much reduced.

Theoretically, we should expect<sup>5</sup> that a certain period elapses from the moment the voltage is applied until a regular deposition of material sets in, so that equation (2) should be violated when the time of the experiments is very short. At low voltages this was actually observed as is illustrated by Table II.

During the first 5 seconds the yield is almost independent of the time and only after about 10 seconds the regular formation of a deposit begins.

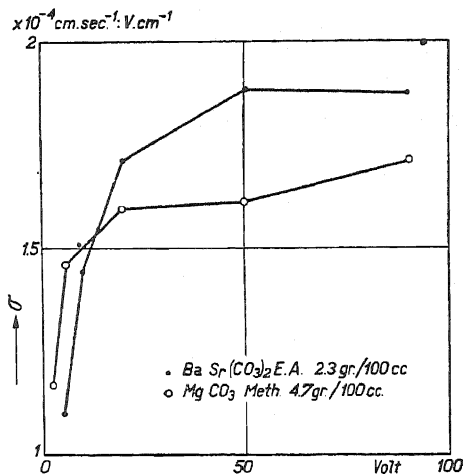


FIG. 5.— $\sigma$  against the voltage.

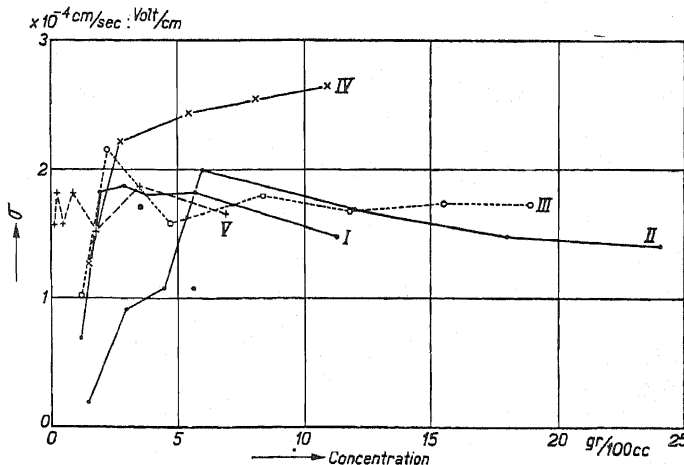


FIG. 6.— $\sigma$  against the concentration.

Our observations showed that when the voltage increases the initial period very rapidly diminishes so that at 50 v. or more, it is entirely unobservable. The time limit to formula (2) does not appear to be of practical importance.

<sup>5</sup> See the earlier article in *this volume*, p. 180.

TABLE II.—BaSr(CO<sub>3</sub>)<sub>2</sub> IN ETHANOL-ACETONE; 4.5 g./100 c.c., 5 VOLTS.

Time.	Yield.	Y/t.	Time.	Yield.	Y/t.
1 sec.	0.6 mg.	0.6 mg./sec.	20 sec.	2.7 mg.	0.14 mg./sec.
2 "	0.6 "	0.3 "	40 "	4.7 "	0.12 "
5 "	0.8 "	0.16 "	80 "	9.9 "	0.13 "
10 "	1.7 "	0.17 "			

#### 4. Theory.

Let us now consider these observations from the point of view of the theory already referred to.

During electro-deposition the coating electrode is surrounded by a region in which the suspension is highly concentrated and sinks by its high density. When the voltage decreases, this zone will become of greater extension since the force on the particles is diminished. Thus at lower voltages the transport of material towards the bottom by convection currents increases with respect to the electrophoretic transport towards the coating electrode, and  $\sigma$  consequently decreases (Fig. 5).

That the fall in  $\sigma$  sets in abruptly is easily understood. For when the voltage is reduced, not only does the extension of the region of higher concentration increase, but also the total surplus of material amassed in this region whereas the electrophoretic velocity diminishes. These three factors therefore co-operate so that the disturbing influence of the convection currents once felt will very rapidly increase when the voltage is still further diminished.

If this explanation is correct, it must be inferred that, so long as equation (2) remains valid, convection currents do not in a measurable degree interfere with the formation of a deposit and  $\sigma$  is practically equal to the electrophoretic velocity. Fig. 5 shows that  $\sigma$  is indeed of the right order of magnitude, though perhaps somewhat lower than usually observed in stable hydrophobic colloids. A direct comparison of  $\sigma$  with the electrophoretic velocity has not yet however been made.

When the concentration is lowered this again will produce a decrease of the electrophoretic particle transport, relative to the removal of particles by convection currents, so that a decrease in  $\sigma$  is to be expected (Fig. 6). Here, however, complications may occur. For with decreasing concentration the electrolytic current increases with respect to particle transport, which will cause a change in the conditions under which electro-deposition takes place.

Finally, from the instant the voltage is applied until the regular layer formation begins, a period elapses in which the region of higher concentration is built up. Thus, the observations recorded in Table II agree with our theoretical considerations.

Altogether we see, therefore, that our theory offers a reasonable explanation of the main features of our experiments. But the phenomena are rather complex, so that we can hardly say that the theory is definitely proved by our observations. To throw more light on these problems would require much more extended observations in which for instance the particle size and the electrolyte content are systematically varied.

In conclusion, it should be mentioned that Patai and Tomaschek in the papers quoted in the introduction, also made some observations on the yield. In some cases they found the yield per coulomb to be constant in agreement with equation (2); in other instances, however, the yield decreases with increasing current density, whereas, we found below 20 v. a yield per coulomb which increases with the current density. The conditions in their colloidal solutions seem to have been different from those in our suspensions.

### 5. The Density.

We have attributed a high theoretical importance to the more or less regular arrangement of the particles in the layer. Hence we expected that a systematic study of the density might yield interesting results in connection with our theoretical considerations. However, our observations in this direction have not produced very conspicuous results, so that we will here mainly describe some experimental methods which may be of value in similar researches.

The density of the layer is easily calculated from the weight of the

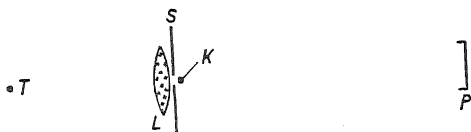


FIG. 7.—Optical arrangement for measuring the diameters of coated electrodes.

TABLE III.—DENSITY OF THE LAYERS.

Substance.	Density of Layer (g./c.c.).	Density of Solid Subst. (g./c.c.).	Ratio.
MgO . . . . .	1.3-1.4	3.6	0.36-0.39
Al <sub>2</sub> O <sub>3</sub> . . . . .	1.9-2.5	4.0	0.48-0.63
CaF <sub>2</sub> . . . . .	1.4-2.0	3.2	0.44-0.63
BaSr(CO <sub>3</sub> ) <sub>2</sub> . . . . .	1.3-2.0	4.0	0.32-0.50
MgCO <sub>3</sub> . . . . .	0.5-0.8	3.0	0.17-0.27

deposit and the diameters of the electrode before and after coating. Systematic measurements of these diameters under a travelling microscope

would require much tedious work, so that we preferred to use an optical method which is sketched in Fig. 7. By the lens L a tungsten spiral lamp T is focussed on a photocell P connected to a galvanometer. Close to the lens a horizontal slit is mounted 2 mm. wide and 20 mm. long. When a coated electrode is brought directly in front of this slit as indicated a portion of the light is intercepted and the galvanometer deflection decreases. The change in the deflection will be a function of the average diameter of the coated electrode so that the latter can be derived from the former. The set up was calibrated by means of a set of standard electrodes which were carefully measured under the microscope. By this device systematic observations on the density could very conveniently be carried out; the mean square error of an optically determined diameter was 4 $\mu$ .

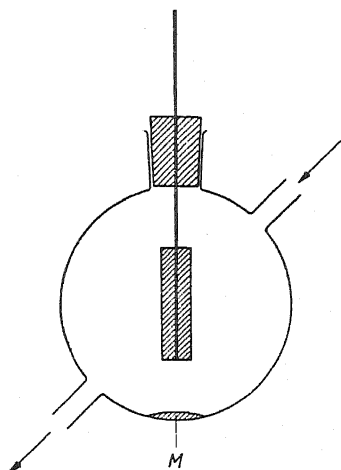


FIG. 8.—Apparatus for observing the shrinkage.

A survey of the densities of the coatings prepared from different substances is reproduced in Table III.

Al<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub> gave the most compact layers, up to 60 per cent consisting of the solid material; the MgCO<sub>3</sub> deposits were of a very loose structure containing not more than 30 per cent. of the solid substance.



The densities recorded in the above table are those of the air-dry layers. These are only representative of the structure of the deposit formed by electrophoresis when the drying has not produced a marked shrinkage of the coating. This point was investigated by the arrangement shown in Fig. 8.

TABLE IV.—SHRINKAGE OF THE LAYERS UPON DRYING.

MgO . . . . .	10 %
MgCO <sub>3</sub> . . . . .	7 %
CaF <sub>2</sub> . . . . .	2 %
BaSr(CO <sub>3</sub> ) <sub>2</sub> . . . . .	0 %

The coated electrode, when still wet, is inserted in a container, the atmosphere in which is saturated through the addition of a few drops M of the dispersive fluid. Thus drying is prevented and the wet diameter is observed under a microscope. Next a blast of air is led through the container as indicated by the arrows and when drying is complete a second observation is made. All the time the apparatus is kept in the same position under the microscope so that both observations are made exactly at the same spot. The amount of shrinkage found was (Table IV).

With BaSr(CO<sub>3</sub>)<sub>2</sub> and CaF<sub>2</sub> the shrinkage was small and these substances were chosen for some more detailed observations. In the MgO layer the shrinkage produced very large cracks but with MgCO<sub>3</sub> no cracks were formed though shrinkage was still considerable. Hence the absence of visible fissures in the dry layer is not a sufficient criterion for the absence of shrinkage.

Further observations with BaSr(CO<sub>3</sub>)<sub>2</sub> and CaF<sub>2</sub> brought to light that the density slightly increases with the thickness of the layer and decreases with the voltage applied. Besides when these two quantities are kept

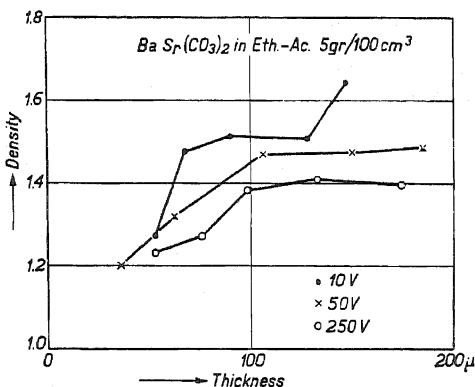


FIG. 9.—Density as a function of voltage and thickness of the layer.

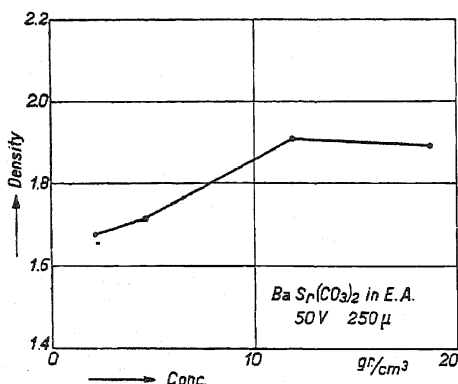


FIG. 10.—Density as a function of the concentration.

constant the density was found to increase with increasing concentration. For BaSr(CO<sub>3</sub>)<sub>2</sub> these results are illustrated by Figs. 9 and 10. Changes in the density upon the addition of electrolytes have also been the subject of some experiments. In some cases the density was fairly constant, in others it diminished when the electrolyte concentration was increased. These observations are too unsystematic, however, to warrant a detailed discussion here.

When the voltage is increased the formation of a

layer will take place with greater velocity which may readily lead to a more irregular structure. Likewise, we should expect the influence of electrolytes which finally coagulate the suspensions to be first manifest from a fall in the density of the electrophoretic coating. The observations

of Fig. 10 are not so easily explainable but here the ratio of the electrolytic current to particle transport may have been a disturbing factor. Our data are too few, however, to attach great value to these theoretical considerations.

It will be evident that Dr. J. H. de Boer upon whose instigation this work was started has followed the experiments with keen interest. Frequent intercourse with him has been of considerable value, for which the author would like to express his gratitude in concluding this paper.

### Summary.

From suspensions in certain organic media, it is possible to apply a coating of the suspended material by electrophoresis. The experimental aspects of this phenomenon are investigated in this paper. Within certain limits the amount deposited is proportional to the time, the surface of the electrode, the electric field and the concentration.

Deviations from this simple law are observed at low voltages, short times, or when the concentration is too low. The deviations observed can be understood from theoretical considerations given elsewhere.

Finally, a simple method for studying the density of the layers is described together with some observations made by it.

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## THE DEPOSITION OF OXIDE COATINGS BY CATAPHORESIS.

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*(Communication from the Research Staff of the M.O. Valve Co., Ltd., at the G.E.C. Research Laboratories, Wembley, England.)*

The particular object of this paper is to describe the experimental work connected with the production of non-colloidal, cataphoretic suspensions of alkaline earth carbonates, and alumina. We believe that the properties of these suspensions, which are of importance in the valve industry, will be of general interest.

The cathode of a modern receiving valve consists of a suitable core-metal, such as nickel or tungsten, coated with a layer of a double oxide of barium and strontium. The core-metal is coated in the first place with a double carbonate which is subsequently decomposed to the oxide when the cathode is heated in vacuum.

The normal methods of applying the carbonate coating depend on the type of cathode, and two methods are in general use. Indirectly heated valves have a cathode consisting of a hollow nickel tube. The coating is sprayed on to the outside of the tube from an organic suspension of carbonate, containing a cellulose binder. Filamentary cathodes, in the form of wire or strip, are coated by being dragged through a series of baths containing a water suspension of carbonate, with a little nitrate added to act as a binder. The coating picked up is sintered after each

bath, and the process is repeated until the required weight of coating is obtained.

The ideal cathode coating should be composed of fine particles ( $\frac{1}{2}$  to 15  $\mu$ ), and should have a smooth surface. It must be sufficiently adherent to permit of a good deal of handling, and the process of application must be capable of close control of coating weight.

It has been proposed to apply the carbonates by cataphoresis from colloidal solutions in methyl alcohol or glycerine and water. Such processes have been described in detail by Patai and Tomaschek,<sup>1, 2</sup> and von Buzágh.<sup>3</sup> These processes apply the coating in one operation, and the coating weight is closely controlled by current density and time.

Our experience with such suspensions has shown them to be unstable. Furthermore, the coatings obtained are soft, and have to be protected by covering them with a film of cellulose or paraffin wax. This method of protection introduces difficulties during pumping.

The heaters used for indirectly heated valves generally consist of tungsten wires fitted into the hollow cathode, and insulated from it by their coating of pure alumina. The methods of applying the alumina are similar to those described for the carbonates.

We have set out to investigate the possibility of preparing concentrated suspensions of alkaline earth carbonates and alumina, from which the particles may be deposited by cataphoresis. In addition, it has been our aim to deposit at the same time a cellulose binder which will give adherent properties to the deposit.

### Experimental.

Our investigations were initiated by an observation that relatively coarse alumina particles could sometimes be deposited by cataphoresis on one of a pair of electrodes immersed in a water suspension of alumina.

A preliminary investigation with aqueous suspensions showed that the cataphoretic behaviour was variable, and the mechanical disturbances, due to the large amounts of gas evolved, made control of the depositions extremely difficult.

Our efforts were then directed to the preparation of suspensions in insulating organic liquids. A Philips' patent<sup>4</sup> states that mechanical dispersions of non-colloidal particles in non-aqueous liquids exhibit cataphoretic properties, and a more recent paper by Gemant<sup>5</sup> describes the cataphoretic deposition of resin particles suspended in insulating liquids.

Our experiments were carried out with barium-strontium carbonate particles of size  $\frac{1}{2}$  to 15  $\mu$ . The carbonate preparation has been described elsewhere.<sup>6</sup>

The alumina used was pure calcined alumina, which had been ball-milled until its particle size was 10 to 50  $\mu$ .

We propose to describe briefly the development of the suspensions, and to deal with their properties in greater detail in the latter half of the paper.

#### 1. Choice of a Liquid Dispersion Medium.

The experimental procedure consisted simply of mixing the carbonate with a liquid. Two metal electrodes were then immersed in the mixture. A potential difference was applied between them, and any deposition of

<sup>1</sup> Patai and Tomaschek, *Koll. Z.*, 1936, **74**, 253.

<sup>2</sup> *Ibid.*, **75**, 80.

<sup>3</sup> Von Buzágh, *Koll. Z.*, 1936, **77**, 172.

<sup>4</sup> *British Patent No. 444723*.

<sup>5</sup> A. Gemant, *J. Physic. Chem.*, 1936, **43**, 743.

<sup>6</sup> Benjamin, Huck and Jenkins, *Proc. Physic. Soc.*, 1938, **50**, 345.

solid on the electrodes noted. A number of common organic liquids was tried, and the results are shown in Table I.

TABLE I.

Liquid.	Dielectric Constant.	Plating.	Remarks.
Ethyl alcohol . . .	23	No	On positive electrode. Suspension variable.
Methyl alcohol . . .	33	Yes	
N. Propyl alcohol . . .	12	No	
Butyl alcohol . . .	17	"	
Amyl alcohol . . .	15	"	
Benzene . . .	2.3	"	
Amyl acetate . . .	4.8	"	
Diethyl oxalate . . .	8.2	"	
Diethyl carbonate . . .	3.1	"	
Glycerine . . .	43	"	
Ethylene glycol . . .	35	"	
Trichlorethylene . . .	—	"	Some deposit on both electrodes.
Acetone . . .	21	Yes	
Water . . .	81	No	
BaCO <sub>3</sub> /SrCO <sub>3</sub> . . .	6 to 7		
Al <sub>2</sub> O <sub>3</sub> . . .	4 to 8		

It will be observed that the only liquids at all suitable appear to be acetone and methyl alcohol. In these liquids, the carbonate was deposited mainly on the cathode, and alumina was deposited on the anode. The methyl alcohol suspensions did not always give reproducible results, but the acetone suspensions appeared to behave consistently.

## 2. The Final Suspension.

The deposition of carbonate from acetone results in a very soft coating. Considerable difficulty was also encountered due to rapid settling of the carbonate particles. The essential requirements for a satisfactory suspension are :—

- (1) The liquid should not evaporate too rapidly.
- (2) Settling should not occur too quickly.
- (3) The resultant coating should be smooth and adherent to the core-metal.

After some experiment with viscous liquids, it was found that the addition of a small quantity of ethylene glycol to the acetone suspension satisfied the first two requirements. It also inhibited the deposition on the anode, and resulted in a smooth coating on the cathode. The deposited coating was, however, still soft.

Good adhesion of the coating was eventually obtained by adding nitrocellulose as a binder. The nitrocellulose is first dissolved in a mixture of diethyl oxalate and diethyl carbonate.

The final formula used for the coating suspension is as follows :—

Carbonates (or alumina) . . .	— 100 g.
Acetone . . .	— 200 c.c.
Ethylene glycol . . .	— 13 c.c.
Nitrocellulose binder . . .	— 200 c.c.

The binder consists of 60 g. of nitrocellulose dissolved in 850 c.c. of diethyl oxalate and 1950 c.c. of diethyl carbonate.

With such a suspension, carbonates are deposited mainly on the positive electrode, instead of on the negative electrode as for the pure acetone suspension. Alumina is still deposited on the positive electrode.

The general properties of the final carbonate suspension are as follows :—

(1) The weight of deposit obtained in a given time is approximately proportional to the current density.

(2) On reversing the potentials of the electrodes, the coating is not completely removed.

(3) After about 30 sec., deposition practically ceases and the current falls. By switching off and then on again, a further deposit is obtained.

(4) A tungsten anode is oxidised during the deposition, but nickel is not visibly affected.

The alumina suspension differs from the carbonate in that no polarising action takes place with time, the deposit is completely removed on reversal, and a tungsten anode is not oxidised.

### 3. Properties of Acetone Suspension.

In the first part of the paper we have given the details of a suspension which exhibits cataphoretic properties.

A suspension of alkaline earth carbonates in acetone exhibits certain features which appear to be due to some composite property of the acetone-carbonate mixture. The main phenomena are listed in Table II. The features may be summarised as follows :—

(1) Pure acetone has a very low conductivity, and there is no visible chemical effect on the electrodes whether nickel or tungsten.

(2) The addition of carbonate increases the conductivity by about a factor of four.

(3) Carbonate particles are deposited on both the negative and positive electrodes initially. After a second or so, gas is evolved at both electrodes and the positive deposit, initially very heavy, is loosened and falls off in a mass. The deposit on the negative electrode continues to build up for about 30 sec. In this period, the current falls to 80 per cent. of its original value, and deposition on the negative electrode practically ceases. On switching off and then on again, the original properties are restored.

When the positive electrode is of an easily oxidisable material (tungsten or molybdenum), oxidation of that electrode occurs. When the positive electrode is oxidised, the original deposition on that electrode is not so easily removed. On reversal, the oxidised electrode is reduced.

When alumina is added to acetone, alumina particles are deposited only on the positive electrode. There is no marked increase in conductivity, and no attack on the positive electrode, and no gas is evolved.

These facts suggest that there is present in the carbonates some slight impurity which is responsible for charging the carbonate particles both positively and negatively. Since the anode (when tungsten) is oxidised and then reduced on reversal, the gases evolved appear to be hydrogen and oxygen.

The possible impurities in the carbonate are very small traces of sodium carbonate and barium nitrate. The addition of small quantities of these to acetone did not result in oxidation of tungsten anodes.

The addition of a small amount of water to the pure acetone suspension has no effect on the tungsten electrode. The presence of a small amount of water has no effect on the behaviour of carbonate suspension.

The addition of small amounts of acid or alkali to pure acetone results in oxidation of the tungsten anode, but appears to have no effect on the properties of the carbonate suspension other than a small increase in conductivity. Large quantities of these impurities inhibit the cataphoretic properties.

TABLE II.—PROPERTIES OF ACETONE SUSPENSIONS.

Suspension.	Electrode Arrangement.	Conductivity.	Deposition.	Effect of Reversal of Applied Potential.	Appearance of Electrode Metal.	Remarks.
Acetone . . .	+					
	Ni. W	1	—	—	Unchanged	No gas evolved at electrodes.
	Ni. W	1	—	—	"	—
	Ni. W	1	—	—	"	—
Acetone 200 c.c. Carbonate 100 g.	Ni. W	4	Initially occurs on both electrodes. After a second or so, gas evolution is apparent at both electrodes and the coating on the positive is loosened. With tungsten as the positive, loosening is not so marked.	Initially the coating is removed from the original negative, but it then builds up again very slowly.	Nickel unchanged. Tungsten anode is oxidised. On reversal, it is reduced.	After 30 seconds, the current is reduced by about 20 per cent., and deposition practically ceases. On switching off and on again, the original properties are restored.
	Ni. W	4				
	Ni. W					
	Ni. W					
Acetone 200 c.c. Alumina 100 g.	Ni. W	1	Deposition occurs only on the positive electrode.	Process is reversed, the original positive electrode is cleaned.	Unchanged.	There is no polarising action.
	Ni. W	1				
	Ni. W	1				
	Ni. W	1				

TABLE III.—PROPERTIES OF ACETONE SUSPENSIONS + ETHYLENE GLYCOL.

Suspension.	Electrodes. +	Conductivity.	Deposition.	Effect of Reversal.	Condition of Electrodes.	Remarks.
Acetone 200 c.c. Carbonates 100 g. glycol 13 c.c.	Ni. Ni. W W Ni. W W Ni.	45 45 45 45	On negative only. The deposit is un- affected by in- creasing quantities of glycol up to 50 % of liquid. The suspension ceases to exhibit cataphoresis after this quantity.	Removes coating and deposit occurs on other electrode.	Ni. unchanged. W oxidises as the po- sitive and reduced on reversal.	Current falls as for acetone.
Acetone 200 c.c. Alumina 100 g. glycol 13 c.c.	Ni. Ni. W W Ni. W W Ni.	45 45 45 45	Deposits always on positive electrode	Reversal complete.	No effect.	Current remains steady.

### The Final Suspension.

In Tables III and IV, we indicate what is to be expected when ethylene glycol and binder suspension are added to the carbonate-acetone mixture.

It is important to note that the results in Table IV apply only when the liquids are first mixed together and then the carbonates added.

The chief features of the preparation of the final suspension are as follows :—

(1) The addition of a small amount of ethylene glycol to the acetone-carbonate results in a marked increase in conductivity, but there is then no evidence of deposition on the positive electrode, except at very low current densities. The tungsten anode is still oxidised, and the negative electrode is coated normally. On reversal of the applied potential, the deposit is not completely removed from the original cathode. Ethylene glycol can be added until its volume is equal to that of the acetone without further effect. When the ethylene glycol concentration exceeds 50 per cent. of the liquid volume, the cataphoretic properties cease.

The addition of the glycol to the alumina acetone suspension has no effect on the cataphoretic properties until its concentration is high when deposition ceases.

(2) The addition of diethyl oxalate or diethyl carbonate singly or

together has no effect on the acetone-carbonate mixture until the concen-

tration is greater than 50 per cent. At this stage, deposition virtually ceases. The addition of binder solution (nitrocellulose in diethyl oxalate and diethyl carbonate) tends to prevent the initial deposition on the negative electrode, and there is no indication of any deposition on the positive electrode.

There is no effect of these materials on the alumina-acetone mixture.

#### 4. The Reversal Effect.

We have stated that the addition of binder solution tends to prevent deposition of carbonates from acetone on the negative electrode and prevents the initial deposition on the positive electrode. The addition of binder solution to the carbonate-acetone-ethylene-glycol mixture sometimes appeared to increase the deposition on the positive electrode, but consistent results could not be obtained.

If, however, the liquid components acetone, ethylene glycol and binder solution are first mixed together and then the carbonate mixed into the liquids, the properties of the original carbonate-acetone mixture are completely reversed. A uniform smooth deposit occurs on the positive electrode, and a slight non-adherent deposit on the negative electrode.\* The positive deposit gives the impression that the binder solution has been deposited with the carbonate, while binder is substantially absent from the negative electrode. The nature of the electrode materials has the same slight effect as in acetone. The use of a tungsten anode, which is oxidised during deposition, gives a very adherent coating indeed. On reversal of the applied potential, the deposit is only partly removed from the original positive electrode. A thin adherent coating, probably due to the reverse deposition, is left.

We have attempted, without success, to decide at exactly what

TABLE IV.—ACETONE + ETHYLENE GLYCOL + BINDER SUSPENSION.

Suspension.	Electrodes. +	Conductivity.	Deposition.	Effect on Reversal.	Condition of Electrodes.	Remarks.
Acetone 200 c.c.	Ni.	45	On positive electrode but slight deposit on negative electrode.	Coating only partly removed.	Ni. unchanged W oxidised as positive electrode.	Up to 200 c.c. of binder can be used. When a large excess of binder, no cathaphoresis.
Glycol 13 c.c.	W	45				
Binder 200 c.c.	Ni.	45				
Carbonates 100 g.	W	45				
Acetone 200 c.c.	Ni.	45	Only on positive electrode.	Complete reversal.	No effects.	Up to 200 c.c. of binder can be used. When a large excess of binder, no cathaphoresis.
Glycol 13 c.c.	W	45				
Binder 200 c.c.	Ni.	45				
Alumina 100 g.	W	45				

\* It is difficult to distinguish between the negative deposit, and pick-up.



point the reversal occurs. The only certain method of securing the remarkably uniform deposits on the cathode is to mix all liquids together first. Suspensions made in this way are quite stable in their properties.

The quantities of each liquid component are not very critical, provided the acetone is not less than 40 per cent. of the total liquid volume.

The alumina behaves in this liquid mixture as it does in acetone, but the deposit on the positive electrode is very adherent, presumably because of the presence of the binder.

### Discussion of Results.

Referring to Table I, one would expect, from the dielectric constants, that the carbonate particles in acetone would be negatively charged. Actually, they appear to be both negatively and positively charged. Immediately after switching on the current a heavy deposit can be obtained on the anode, but subsequent deposition occurs almost exclusively on the cathode. It may be that the evolution of gas at the anode prevents adhesion of the coating. An attempt to observe the motion of the particles under the microscope was unsuccessful. The mechanical disturbances of the liquid prevented the cataphoretic motion of the particles from being discerned.

Alumina, having a dielectric constant similar to that of the carbonates, follows Coehn's Rule, being deposited on the anode.

The failure of small additions of various possible impurities to affect the behaviour of pure acetone, suggests that the carbonate itself, when suspended in acetone, may be the source of ions which confer both kinds of charge on the suspended particles.

The reversal in the final suspension is peculiar. The carbonate particles show no charge effect when suspended in the separate components other than acetone. The presence of acetone in a suspension of carbonates in each of the other component liquids results in cataphoretic properties. The best deposit is obtained on the cathode. When nitrocellulose is present the deposition occurs entirely on the anode.

Tantz and Pickett<sup>7</sup> have found that nitrocellulose in amyl acetate, or acetone, shows cataphoresis; and that the nitrocellulose is negatively charged. Our observation that the binder is deposited on the anode is probably explained by this fact. In addition, it seems reasonable to suppose that the presence of negatively charged nitrocellulose is the cause of the reversal of the charge on the carbonate particles in acetone.

A direct experiment made by preparing a suspension of carbonates in acetone containing nitrocellulose appeared at first to give only anodic deposition. On standing, however, deposition occurred on the cathode.

These properties of the final suspension appear to be quite stable over long periods of time. As we have stated, alkaline earth carbonates and alumina can be deposited as firm yet flexible coatings on the anode. The particle size does not appear to be important within the range  $\frac{1}{2}$  to 150 microns. We have also found that willemite is deposited from the various suspensions in a manner similar to that of the carbonates. Carbon and carborundum particles behave in the same way as the alumina particles.

Acetone appeared to be superior to other liquids as the suspending medium. A preliminary survey of possible groups of organic liquids (*viz.*, alcohols, ketones and aldehydes) indicates that the higher aliphatic aldehydes, namely paraldehyde and butyric aldehyde, also

<sup>7</sup> Lantz and Pickett, *Ind. Eng. Chem.*, 1930, 22, 1309.

have some of the desired properties. In particular, suspensions in *n*-butyric aldehyde always give deposits on the anode, and addition of nitrocellulose binder results in an adherent coating.

In general, we have been left with the impression that insulating materials can be deposited cataphoretically from non-colloidal suspensions in certain organic liquids.

In conclusion, the authors desire to tender their acknowledgments to the Marconi Co. Ltd. and The General Electric Co. Ltd., on whose behalf the work was carried out.

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## WETTING AND FLOTATION IN CONNECTION WITH THE PROBLEM OF THE TRANSITION LAYER.

By P. REHBINDER.

*Received 10th August, 1939.*

### 1. Wetting and Flotation—Hysteresis of Contact Angle and Wetting Isotherms.

The froth-flotation process (the most widely used process in ore concentration) may be defined from the physico-chemical standpoint as resulting from the selective adhesion (based on molecular interaction) of suspended mineral particles to gas bubbles forming in the aqueous dispersion medium. These mineralised bubbles, rising to the surface of the pulp in the flotation machine, form a mineralised froth, giving a flotation concentrate. This process is mainly conditioned by the incomplete wetting of a given particle by the aqueous medium, *i.e.*, by the formation, upon contact of this particle with an air bubble, of a perimeter of wetting—a three phase line of contact: solid particle—aqueous medium—air bubble. The conditions for wetting (the magnitude of the contact angle and its possible hysteresis) are determined by the molecular nature and the roughness of the solid surface and, very sensitively, they reflect changes in its molecular nature; this makes possible the sharply expressed selectivity of flotation; the fundamental advantage of the modern flotation process. This is determined by the considerable changes in the wettability under the influence of the adsorption of flotation reagents which are soluble in the aqueous medium containing the suspended mineral particles. The surfaces of these particles are covered with adsorption layers of various types.

We have shown that the flotation reagents may be rationally classified according to the nature of the adsorption layers which they form on various solid surfaces and according to the changes in the wettability ( $B = \cos \theta$ , where  $\theta$  is the contact angle) caused by these layers under conditions of maximum hysteresis, *i.e.*, by determining wetting isotherms giving the dependence of wetting upon adsorption or concentration.<sup>1, 2</sup>

<sup>1</sup> P. Rehinder, *VI All-Russian Phys. Congr.*, Moscow, 1928; *J. Physic. Chem. (Russ.)*, 1930, 1, (4/5), 575; P. Rehinder, M. Lipetz, M. Rimskaja and A. Taubmann, *Physical Chemistry of Flotation*, Monograph (in Russian), Moscow, 1933; *Koll. Z.*, 1933, 65, (3), 268; P. Rehinder, M. Lipetz and M. Rimskaja, *ibid.*, 1934, 66, (1), 40; 1934, 66, (2), 212; 1934, 66, (3), 273; M. Lipetz and M. Rimskaja, *ibid.*, 1934, 68, (1), 82.

<sup>2</sup> *New contributions to the Theory of Flotation*, edited by P. Rehinder (in Russian), Moscow, 1937; Rehinder, *Bulletin Acad. Sci. U.R.S.S.*, ser. chim., 1936, 5, 707.

By such a method, we may also estimate quantitatively the flotation effect of each reagent upon the given mineral.

An analysis of two problems of the theory of capillarity connected with flotation, established the fundamental role of the contact angle in the adhesion act of the flotation process. These problems were: (1) The flotation of heavy particles which are not completely wettable on the surface of a liquid (water) (Valentiner, Schranz, and others<sup>3, 4</sup>; and (2) the adhesion of a bubble to a particle within the liquid phase with the subsequent formation of a wetting perimeter.<sup>5, 6</sup>

Let the side surface of a particle [3] which intersects the interface liquid [1]—gas [2] along the wetting perimeter form an angle  $\phi$  (angle of "shape") with the vertical. Then the vertical component of the surface tension  $\sigma_{12}$  (liquid gas) along the perimeter of wetting  $L$  (in dynes/cm.) is given by the following:—

$$f = \sigma_{12} \cdot \cos(\theta + \phi) \quad . \quad . \quad . \quad (1)$$

In the simplest abstract case ( $\phi = 0$ , i.e., the side surface is that of a verticle cylinder), we have

$$f_0 = \sigma_{12} \cdot B \quad . \quad . \quad . \quad (2)$$

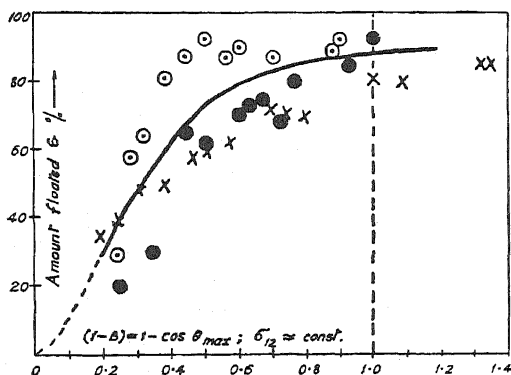


FIG. 1.—Increase in the amount floated with a decrease in wetting

$$\epsilon = \epsilon(1 - B)$$

( $\sigma_{12} \approx \sigma_0 = \text{const.}$ ). Collector—butyl xanthate. (B. Mantzew's data.)

○ activated sphalerite (ZnS).

● pyrite (FeS<sub>2</sub>).

× phosphate ore (Vjatka) with sodium oleate. (M. Bruyère's data.)

This gives a physical meaning to the *wettability*,  $B$ . Actually, flotation (according to (1)) is possible at any contact angle greater than zero [ $\theta + \phi > 90^\circ$ ]. The probability that a particle and a bubble will stick together  $W \sim \exp. \left( -\alpha \frac{\Delta F}{\kappa T} \right)$ , is determined by the decrease in free energy during the adhesion process,  $-\Delta F$ , which in the simplest case\* may be expressed as follows (in ergs./cm.<sup>2</sup>)

$$-\Delta F = \sigma_{12}(1 - B) \quad . \quad . \quad . \quad (3)$$

Here the value  $B = +1$  corresponds to the absence of a three phase contact on the surface of a particle, i.e., to the absence of flotation. The probability of the flotation of a particle, i.e., of its adhesion to a bubble, generally increases with a decrease in the wettability  $B$  and decreases with a decrease in the surface tension  $\sigma_{12}$  of the aqueous medium.

<sup>3</sup> S. Valentiner, *Metall u. Erz*, 1914, 11, 455; *Physik. Z.*, 1914, 15, 425.

<sup>4</sup> Z. Wolkowa, *Koll. Z.*, 1934, 67, 280; *Acta Phys. Chim., U.R.S.S.*, 1936, 4, 635; *J. Physic. Chem. (Russ.)*, 1939, 13, No. 2, 224.

<sup>5</sup> I. Wark, *J. Physic. Chem.*, 1933, 37, 623.

<sup>6</sup> B. Kabanow and A. Frumkin, *Z. physik. Chem., A*, 1933, 165, 433; 166, 316.

\* Wetting hysteresis introduces one more term into the expression for  $-\Delta F$ .

Fig. 1 shows the increase in the amount floated ( $\epsilon$ ) for various pure minerals and reagents as a function of  $1 - B = 1 - \cos \theta_{\max}$ . (see below) at  $\sigma_{12} \approx \sigma_0 = \text{const.}$

The reagents which cause a decrease in the wetting of solid particles by the aqueous medium—"hydrophobisation," under the influence of the adsorption layer formed on them (flotation collectors) always increase the floatability to that point until they begin to lower the surface tension  $\sigma_{12}$  of the aqueous medium of the pulp (suspension) noticeably. On the other hand, flotation reagents which do not cause noticeable changes in the wettability of mineral particles and which are adsorbed mainly at the interface aqueous medium gas are frothing agents. They stabilise the film which forms between those bubbles which approach one another and thus prevent their coalescing, *i.e.*, increase the stability of an emulsion

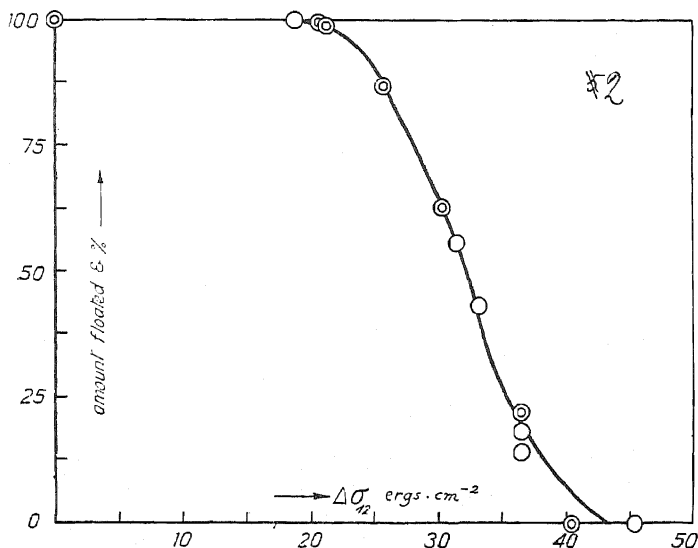


FIG. 2.—The "Toxic" action of the decrease in surface tension ( $\Delta\sigma_{12}$ ) upon skin-flotation (relative amount of powder  $\epsilon = f(\Delta\sigma_{12})$  retained on the surface of an aqueous medium). (M. Lipetz's data.)

- Sulphur on aqueous solutions of iso-amyl alcohol.
- ⊙ Talc on aqueous solutions of heptylic acid.

of air bubbles in an aqueous medium and, furthermore, the stability of the froth. When surface active reagents, both collecting and frothing agents, *e.g.*, soap-like substances, are present in excess, they always lower  $\sigma_{12}$  and, consequently, lower the floatability. It should be noted that a considerable lowering of the surface tension not only decreases the first factor in (3) but also decreases the value of the second factor ( $1 - B$ ), because liquids with a sufficiently low surface tension wet all solid surfaces (Fig. 2).\*

The development (since 1920) of froth-flotation directed attention to the purely chemical side of the process. American investigators,

\* Furthermore, an excess of the collector in the pulp may lead to super-oiling as a result of the formation of a polymolecular adsorption film on the mineral surface, for instance upon the jellification of the adsorption layers of soaps at considerable concentrations.

headed by Taggart and Gaudin,<sup>7, 8, 9</sup> specially studied the chemical reactions which take place between the surface of a mineral and a solution of a flotation reagent. They pointed out the important role and the diversity of such reactions which lead to the formation of insoluble films on the surface of mineral particles, capable of sharply changing the molecular nature of this surface, or which lead to the baring of fresh surface of the mineral.

However, surface chemical reactions in flotation should not be studied separately from the physical effects which they produce, and which determine the conditions of adhesion.

In our work, started in 1928,<sup>1</sup> we studied \* various surface reactions under the influence of flotation reagents by employing a method which is based on measuring the changes in the wettability brought about, starting with typical oriented adsorption, passing to adsorption layers chemically fixed by means of polar groups, and ending with true chemical surface compounds which form sufficiently thick films of a new covering on the surface of the floated particles. The determination of wetting isotherms permits a detailed investigation of the adsorption (e.g., the degree of its irreversibility †) of a reagent on a given mineral surface according to the change in the wettability due to adsorption and directly connected with the act of adhesion.

We arrived at the following conclusions from these experiments: There exists a sharp distinction between two types of oriented adsorption layers: surface active organic substances, giving completely reversible adsorption on the solid surface, without any traces of chemical interaction (e.g., alcohols), exhibit no noticeable decrease in wetting at the boundary solid—water—air. Surface active substances (e.g., fatty acids, xanthates, aerofloats), the polar groups of which may react chemically, uniting with the surface atoms of the metal in the crystal lattice of the floated mineral, give "chemical fixation" of the adsorption layer. This phenomenon, which we subjected to detailed study, consists, evidently, in a strengthening of the normal orientation of the hydrocarbon chains of the non-polar part of the adsorbed molecules. The chains do not bend and therefore increase the resistance offered to a shift of the wetting perimeter of a bubble or a drop of water normal to the perimeter; they therefore cause a sharp lowering in the hysteresis wetting.<sup>2</sup> This was proved by our experiments on shifting the perimeter, e.g., upon decreasing (by sucking out) the volume of a gas bubble which has formed

<sup>7</sup> A. Taggart, G. del Giudice and O. Ziehl, *Trans. Am. Inst. Min. Met. Eng.*, 1935, 112, 348.

<sup>8</sup> A. Gaudin, *Flotation*, N.Y., Lond., 1932.

<sup>9</sup> W. Petersen, *Schwimmaufbereitung*, Dresd.-Lpz., 1936.

\* In these investigations we also drew attention to the significance of the selective wetting by two immiscible, anti-polar liquids (water-hydrocarbon) for a molecular, quantitative classification of solid surfaces as hydrophile or hydrophobe.<sup>1, 2</sup>

† To study this, the adsorption layer which has formed on a plate is washed in a large volume of water while carefully and rhythmically moving the plate up and down for a definite time. By changing the time of washing, we studied the kinetics of desorption. While in these experiments the layers of surface active substances not showing chemical fixation and not giving collector action are washed off immediately, the adsorption layers of the chemically fixed flotation collectors (fatty acids and xanthates) were found, according to measurements of the wettability, to be stable with respect to washing off. The kinetics of the washing off of an adsorption layer gives a new, interesting classification of flotation reagents in complete agreement with that according to the hysteresis wetting isotherms.

in a solution of the given reagent under the solid surface (Fig. 3). This "chemical fixation" is characteristic just for collector action in flotation and guarantees the sticking together of the floated particles and air bubbles.

The formation of such collector adsorption layers results in the "fixing" of the wetting perimeter, which causes an increase in the contact angle. This takes place upon sucking out gas from the bubble sticking to the solid surface (Fig. 3) from the minimum (equilibrium) value  $(\theta_{21})_{\min.}$  to the limiting hysteresis value  $\theta_{\max.} = \theta_{12} = \arccos B_{12}$ . The latter ( $B_{12} = \cos \theta_{12}$ ) corresponds to the case of a drop of water [1] in air [2] on a dry surface of the same mineral preliminarily subjected to adsorption of the collector from the given solution.\* A similar process also occurs in the case of actual flotation when the mineral particles (covered with chemically fixed, oriented adsorption layers) and air bubbles, moving with respect to one another, come into contact. When

FIG. 3.—A study of wetting hysteresis in the presence of collector adsorption layers according to the method of sucking out air from a bubble.

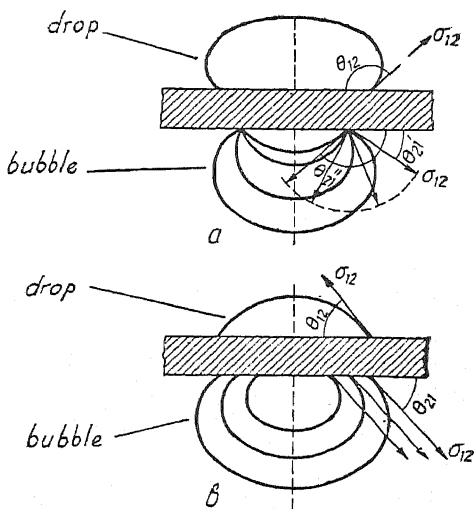
- a. Collector adsorption causing fixation of the perimeter of wetting and rotation of the vector  $\vec{\sigma}_{12}$  to the limiting angle

$$\theta'_{21} - \theta'_{21} = \theta_{\max.} - \theta_{\min.}$$

Above there is represented a drop of water on a dry surface covered with the same adsorption layer which gives the maximum contact angle  $\theta_{12} \approx \theta_{\max.}$

- b. Action of depressing agents and flotation poisons. The wetting perimeter is not fixed; wetting hysteresis is absent; and upon decreasing the volume of the bubble

the vector  $\vec{\sigma}$  does not change its direction:  $B_{21} \approx B_{12}$ .



a particle falls out of a bubble, the contact angle sharply increases up to the limiting hysteresis value as a result of "fixing" of the perimeter of wetting, completely insuring stable union between a mineral particle and a bubble. The vector of the surface tension  $\vec{\sigma}_{12}$  at the wetting perimeter, the numerical value of which remains practically the same, rotates under the influence of flotation collectors with an increase in  $\theta$ , while in the absence of a collector adsorption layer for hydrophile mineral particles, and also during the action of depressing agents, this vector does not change its direction and  $\theta_{21}$  remains constant  $\approx 0$  (Fig. 3), e.g., for galena (PbS) in a 0.01 per cent. butyl xanthate solution, upon sucking out air from a bubble the contact angle increases from  $\theta_{\min.} = 49^\circ$

\* According to the notations which we adopted previously,  $B_{12} = \cos \theta_{12}$  corresponds to a drop of the phase [1] (water) in the medium [2] (gas or non-polar liquid), and  $B_{21} = \cos \theta_{21}$ , to a drop of the phase [2] in the medium [1]. Thus the hysteresis value  $h = B_{21} - B_{12}$  gives us the influence of the order of wetting.<sup>1, 2</sup>

to  $\theta_{\max.} = 135^\circ$  (wetting perimeter fixed), and upon further decreasing the volume,  $\theta_{\max.}$  remains constant, *i.e.*, the wetting perimeter is shifted (see Fig. 1a). Depressing galena with chromate solutions, which already becomes noticeable at  $10^{-4}$  to  $10^{-3}$  per cent.  $K_2Cr_2O_7$ , eliminates this phenomenon.

We may write the following expression for the limiting (maximum) contact angle  $\theta_{\max.}$ , corresponding to the beginning of shifting of the "fastened" wetting perimeter:

$$\cos \theta_{\max.} = \frac{\sigma_{23} - \sigma_{13}}{\sigma_{12}} - \frac{\chi}{\sigma_{12}}; \chi = \sigma_{12} \cdot h \quad (4)$$

Here  $h = B_{21} - B_{12}$  is the limiting-maximum-value of the hysteresis of wetting, and  $\chi_{\max.}$  is the resistance (yield value), analogous to static friction, in dynes/cm. along the perimeter. The largest value of the hysteresis,  $h = B_{21} - B_{12}$  (*i.e.*, the largest deviation between the iso-

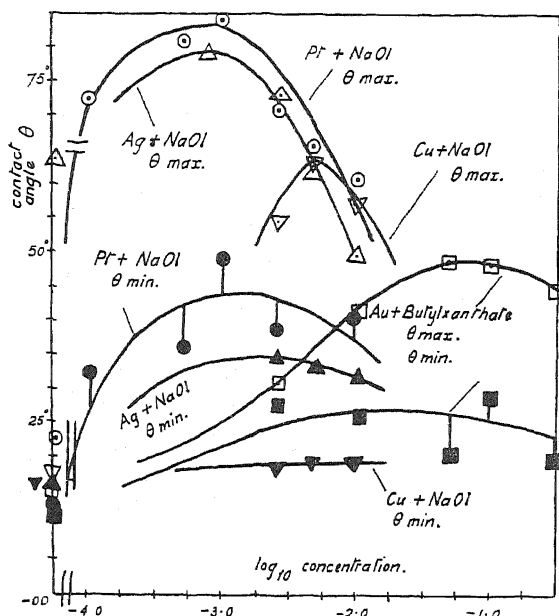


FIG. 4.—Wetting isotherms for oxidized, polished platinum, silver and copper surfaces in aqueous solutions of sodium oleate and gold surfaces in aqueous solutions of potassium butyl xanthate, showing maximum and minimum contact angles (L. Solovjeva's data).

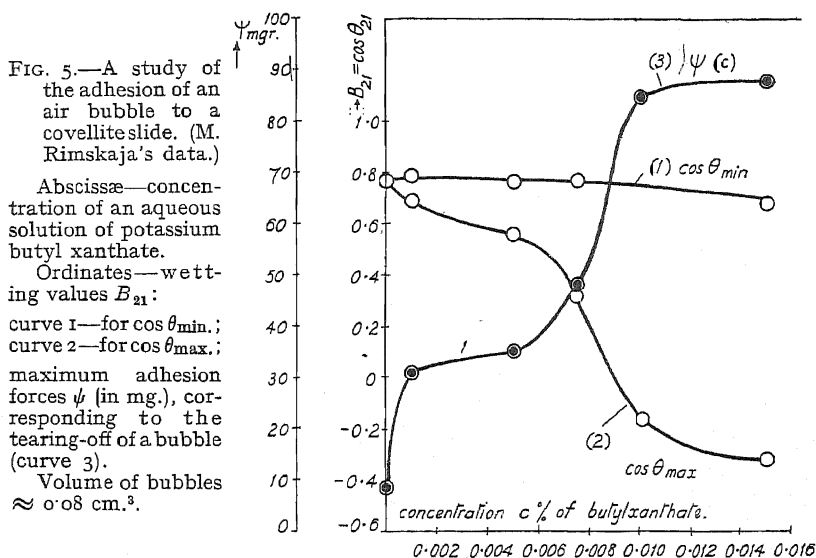
therm  $B_{21} = f_{21}(c)$  and the hysteresis wetting isotherm  $B_{12} = f_{12}(c)$ , is attained upon saturation of the oriented adsorption monolayer of the reagent on the solid surface.<sup>1, 2</sup>

A decrease in the wettability of the solid surface by water occurs in the case of normal orientation of the surface active molecules, *i.e.*, when the polar groups are bound to the surface atoms of the solid (a decrease in free surface energy equal to  $a$  erg./cm.<sup>2</sup> corresponds to such a binding). Meanwhile the hydrocarbon chains of the adsorbed molecules become oriented normal to the surface, forming a hydrophobe outer face which borders on water; this produces an increase in free surface energy equal to  $b \approx 50$  ergs./cm.<sup>2</sup> In the sum total, the formation of such a layer with a hydrophobe outer face is accompanied, naturally, by a decrease in free surface energy equal to  $\Delta\sigma_{31} = a - b$ .

Such an orientation, when  $a$  is sufficiently large, ensures flocculation and flotation (with removal of the hydrated film), caused by the linking

of the hydrocarbon chains which thus squeeze out the water from between them.

In this connection we developed a method of studying the floatability by measuring the contact angle on real solid surfaces under conditions which most closely correspond to the act of adhesion during flotation. One of the shortcomings of Wark's "zero method,"<sup>10</sup> besides the fact that it does not give a continuous change in  $\theta$  with adsorption, consists in that, that Wark does not take into account the time of contact observed by I. Sven Nilsson.<sup>11</sup> We obtained curves giving the increase in  $\theta$  with the time of contact. Such investigations are very laborious and therefore it is more reasonable to employ the method which we call the "method of maximum and minimum contact angles": A bubble is pressed to the solid surface by means of a paraffined holder which is moved vertically with a micro-screw until a contact angle is formed, if this should occur. Then, following the projection of the contour of



the bubble on a screen, the minimum initial value ( $\theta_{\min.}$ ) is measured and, whilst continually stretching the bubble by moving the holder, the maximum value ( $\theta_{\max.}$ ). (Figs. 4, 5.)

As our measurements on real surfaces show,  $\theta_{\max.}$  (the hysteresis value of  $\theta$ ) characterises the decrease in wetting of the surface exceptionally well, while the initial values of  $\theta_{21}(\theta_{\min.})$ , which Taggart obtained, often disclose no significant changes whatsoever\*<sup>2</sup> (Figs. 4, 5).

Thus it is just this maximum value of  $\theta$  which is characteristic for flotation, a value which appears when attempts are made to displace the

<sup>10</sup> I. Wark and A. Cox, *Techn. Publ. A.M.M.I.*, 1933, No. 495; I. Wark, *Rep. Melbourne Meeting Austral. and New Zealand Assoc. adv. Sci.*, 1935.

<sup>11</sup> I. Sven Nilsson, *Koll. Z.*, 1934, 69, 230; *Proc. Roy. Swed. Inst. Eng. Res.*, 1935, No. 133.

\* Taggart and his followers did not make systematic measurements of the wetting isotherms, which may give valuable indications with respect to the optimum conditions for flotation. The expression employed by Taggart for his "collecting index" has no physical meaning.<sup>1, 9</sup>



contact perimeter, for example in our experiments on sucking out (decreasing the volume of the adhering bubbles), and corresponds to the maximum force necessary to tear off the bubble \* (see Fig. 5).

Therefore it is clear that the values of  $\theta_{12}$  for a drop on a dry surface, preliminarily prepared by adsorption from the given solution, often characterise the flotation properties better than the initial (minimum) values of  $\theta_{21}$  after adhesion.†

## 2. Kinetics of Adhesion and Film Thinning.

A. Frumkin<sup>12</sup> was the first to point out the special significance of the kinetics of adhesion of a gas bubble to a solid particle for the mechanism of flotation (similar to the sticking together of primary particles in suspension (flocculation)). Upon the approach of two solid particles or of a particle and a bubble, the liquid film which separates them, and is the fundamental stabilising factor, gradually becomes thinner. According to his views such wetting films with thicknesses comprising a small number of molecular layers may be thermodynamically unstable and will burst, leaving a thinner, stable film; this corresponds to adhesion of the bubble with the formation of a definite contact angle on the interface gas bubble-solid. He further developed a thermodynamic theory<sup>13</sup> which defines the region of stability and the conditions for the appearance of a finite contact angle in terms of the dependence of the surface energy of the film upon its thickness.

Frumkin<sup>14</sup> and his co-workers showed experimentally that a thin film of the aqueous medium, consisting of a few molecular layers, remains between the surface (the surface of mercury) and the air bubble adhering to it, even after the formation of quite large contact angles. It is only for sufficiently thick, stabilising films (studied by Derjaguin),<sup>15</sup> that contact angles are not formed (complete wetting); this corresponds to the absence of adhesion of the bubble, i.e., "no contact" according to Wark.<sup>10</sup> Further, Kabanow showed that the "remaining contact film" becomes thinner with an increase in the contact angle.<sup>16</sup>

Further elucidation of the process of film-thinning follows from the study of the thermodynamic behaviour of comparatively thick wetting films, made by Derjaguin and Kussakov.<sup>15</sup> For this a new method was specially developed which consists in a measurement of the equilibrium thicknesses  $h$  of the wetting films and the corresponding capillary pres-

\* It is sometimes more convenient to measure the value of the force necessary to tear off a bubble of a definite size slowly (see Fig. 5) instead of the maximum value of  $\theta_{21}$ .

† The contact angle of a drop ( $\theta_{12}$ ) for rough solid surfaces represents the upper limit of the value of  $\theta_{21}$ , i.e., the value  $B_{21} - B_{12} = h$  gives us the upper limit of the possible values of the hysteresis.

On smooth polished surfaces the hysteresis of wetting, i.e., the difference  $h = B_{21} - B_{12}$ , becomes much smaller.

<sup>12</sup> A. Frumkin, *Physical Chemical Fundamentals of the Theory of Flotation, Trans. of the Ural-Kusnetzh conference of the Acad. Sci. of the U.S.S.R. (in Russian)*, Leningrad, 1932.

<sup>13</sup> A. Frumkin, *Acta phys.-chim. U.R.S.S.*, 1938, 9, No. 2, 313.

<sup>14</sup> A. Frumkin, A. Gorodetskaja, B. Kabanow and N. Nekrassow, *Sov. Phys.*, 1932, 1, 255; A. Frumkin and A. Gorodetskaja, *Acta Phys. Chim., U.R.S.S.*, 1938, 9, No. 2, 327.

<sup>15</sup> B. Derjaguin and M. Kussakov, *Bull. Acad. Sci. U.R.S.S., sér. chim.* 1937, 5, 1153; *Acta Phys. Chim., U.R.S.S.*, 1936, 5, 1; 1939, 10, No. 3, 333; B. Derjaguin and M. Kussakov, *Bull. Acad. Sci. U.R.S.S., sér. chim.*, 1936, 5, 741; 1937, 5, 1119.

<sup>16</sup> B. Kabanow and N. Ivanishenko, *Acta Phys. Chim., U.R.S.S.*, 1937, 6, 701.

tures  $P$  which, acting within a bubble placed below the surface, tend to make the separating (wetting) film thinner. The equation of state for the wetting film,  $P = P(h)$ , *i.e.*, the isotherm of its "disjoining" \* pressure  $P(h)$ , shows deviations from the properties of a volume phase. These deviations become noticeable for values of  $h$  of the order of  $0.1\mu$ , *e.g.*, for a wetting film of water on mica.<sup>15</sup> The shape of such isotherms is similar to that of a van der Waals isotherm for a real gas and explains the phenomenon of film bursting, with the formation of a contact angle different from zero, by indicating the existence of a region of unstable states (thicknesses) of wetting films.

According to the measurements carried out by Derjaguin and Kussakov,<sup>15</sup> dissolved electrolytes and surface active non-electrolytes may have quite a marked influence both upon the shape of the pressure isotherm of the wetting film and upon the mechanical properties of the film, especially at small thicknesses (in the neighbourhood of the region of unstable states), changing the conditions of film rupture and the value of the contact angle formed. As they showed on the basis of a simple experiment, this equilibrium pressure of wetting films cannot be ascribed to the action of van der Waals forces, *e.g.*, of the London dispersion forces. It is possible also to reduce these forces to electrostatic and osmotic effects which depend upon the ions present in the solution. Such computations for  $P(h)$  of electrolyte films, made by Derjaguin on the basis of the theory of strong electrolytes and the simplified Debye-Hückel equation, showed that such an explanation of this effect is invalid for average and high concentrations of electrolytes.

Computations adapted to the case of wetting films and carried out on the basis of the exact Debye-Hückel equation were then made by Frumkin,<sup>14</sup> and by Langmuir.<sup>17</sup> The equation so obtained shows<sup>14</sup> that the thickness of the wetting film at constant  $P$ , *i.e.*, at constant dimensions of the bubble, should have been proportional to  $c^{-\frac{1}{2}}$  (where  $c$  is the electrolyte concentration). This conclusion, however, according to Derjaguin and Kussakov, is in sharp contradiction to experiment: while for small  $c$  (of the order of  $10^{-4} - 10^{-5}$  N.) there is approximate agreement between theory and experiment, upon an increase in  $c$  the experimental value of  $h$  falls very slightly, reaches a minimum, and then increases; while the theoretical value of  $h$  continuously falls with an increase in  $c$ , becoming 100 times smaller than the experimental value at  $c$  of the order of  $0.1$  N.

These experiments therefore point to the existence of forces which do not fit into the framework of the Debye-Hückel theory—solvation forces (acting also in absence of any ions, *e.g.* in hydrocarbon media) which are evidently unconnected with the direct electrostatic interaction of ions (see also <sup>14</sup>).

The thick layers studied by Derjaguin are formed only in the case of the marked solvation of a solid surface by the liquid and this corresponds to complete wetting, *e.g.*, for hydrophile surfaces (in the case of water). On the other hand, in the case of more hydrophobe surfaces we immediately enter, according to Frumkin, the region of labile thicknesses of water films between a bubble and a surface, which corresponds to a more or less rapid thinning of the film, with formation of a definite

\* The "disjoining" (wedging) action  $P(h)$ , according to Derjaguin,<sup>15</sup> conditions stabilisation, *i.e.*, the resistance of the particles or particles and bubbles to aggregation.  $P(h)$  decreases with an increase in the film thickness  $h$ , but it is still quite noticeable at  $h < 0.1\mu$ .

<sup>17</sup> I. Langmuir, *Science*, 1938, 88, (2288), 430, *J. Chem. Physics*, 1938, 6, 873.

contact angle, *i.e.*, with clearly expressed rupture and formation of droplets of the aqueous phase on the area of contact bubble-mercury covered by a very thin "contact film."<sup>14</sup> Frumkin's investigations allowed him to explain the interesting observations\* made by I. Sven Nilsson<sup>11</sup> who showed that the "induction" time of preliminary contact of the mineral surface with a bubble, which is necessary for adhesion, *i.e.*, for the formation of a finite contact angle, is a measure of the readiness of the mineral for flotation. This time, which varies within very wide limits, decreases as a result of the adsorption of the flotation collectors† and increases to infinity under the influence of depressing agents or flotation poisons which form sufficiently thick, stable, transition films.

### 3. The Role of the Electric Double Layer in Flotation.

At the boundary, liquid-gas, the electric potentials do not play any considerable role. On the other hand, on mineral surfaces where these potentials may be very great, they are extremely important for an understanding of the action of electrolytes, *viz.*, the regulating reagents (flotation modifiers), most significant for selective flotation.

The solution of these problems is connected with the theory of electrocapillary phenomena (Gouy<sup>18</sup> and Frumkin<sup>19</sup>). Frumkin developed a simple quantitative theory to explain the general phenomenon of the decrease in the adsorption of surface active molecules under the influence of a double layer. A charging of the interface to the potential difference  $\phi$  is equivalent to a dilution of the solution in the ratio  $\exp. \frac{\Phi \cdot S}{\kappa T}$ , where

$\Phi S = \frac{1}{2} c \phi (\phi - 2\phi_N) S - \Delta_e \sigma \cdot S$  is the change in the molar work of adsorption under the influence of the electric field;  $C$  is the capacity of the double layer at limiting adsorption of neutral molecules ( $S$  is the area per molecule);  $\phi_N$  is the potential difference (determined by molecular dipoles only) at the maximum of the electrocapillary curve, *i.e.*, for an uncharged surface; and  $\Delta_e \sigma = \frac{1}{2} C_0 \phi^2$  (in the simplest case, when  $C_0 = \text{const.}$ ) is the "pure electric" decrease of the interfacial tension.<sup>19</sup> This effect is connected with the forcing out (similar to a "salting out") of a substance having a small dielectric constant from the double layer.

This shows that the adsorption of neutral collectors, and, consequently, flotation, has a maximum at the maximum of the electrocapillary curve, *i.e.*, at the isoelectric point. This was experimentally shown by Talmud,<sup>20</sup> for the case of the flotation of  $\text{BaSO}_4$  and  $\text{AgI}$ . The charging of the particle surface, *i.e.*, a change in the concentration of the ions which form the double layer, causes a decrease in collector adsorption, *i.e.*, in flotation, on both sides of the iso-electric point.

Polarisation of the surface, *i.e.*, receding from the maximum of the electrocapillary curve on both sides, causes an increase in wetting and a corresponding thickening of the "contact film" in the absence of surface active molecules also, which gives a decrease in the adhesion of

\* Unfortunately, no one as yet has attempted to repeat these observations or to develop them further.

† The role of the collector adsorption layer consists in a thinning of the contact film,—its transition into the unstable region.

<sup>18</sup> G. Gouy, *Ann. Physique*, 1917, 7, (9), 175.

<sup>19</sup> A. Frumkin, *Z. Physik*, 1926, 35, 792; *Erg. exact. Naturwissensch.*, 1928, 7, 235; *Coll. Symp. Ann.*, VII, 1930, 89, N.Y.; A. Frumkin and A. Obrutschewa, *Biochem. Z.*, 1927, 182, 220.

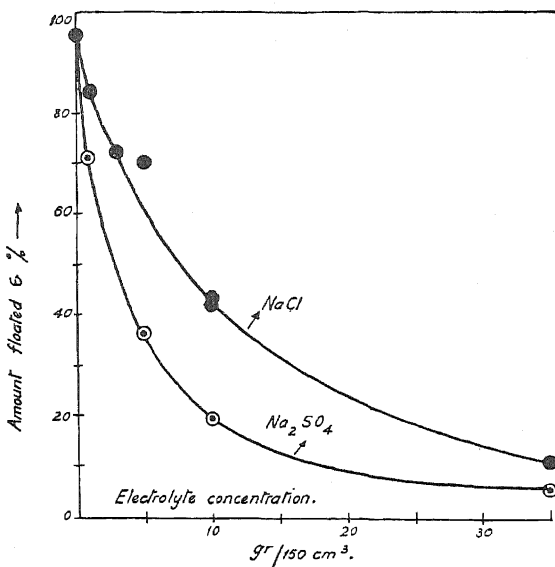
<sup>20</sup> D. Talmud, *Koll. Z.*, 1929, 48, 165; D. Talmud and N. Lubmann, *ibid.*, 1930, 50, 159.

bubbles or oil droplets, *i.e.*, a decrease in flotation (Frumkin and co-workers<sup>14</sup>).

Our measurements on the effect of neutral electrolytes (up to high concentrations) upon flotation illustrate these relations very well (see Fig. 6). This is of interest for the flotation of soluble salts from their saturated solutions. In all these cases the considerable decreases in the

FIG. 6.—The inhibiting action of neutral electrolytes (*i.e.*, of the electrical double layer) upon collector action in flotation.

Flotation of barytes (15 g.—200 mesh in 150 cm.<sup>3</sup> of water) in a M-S laboratory machine by oleic acid (0.03 cm.<sup>3</sup> of a 1 per cent. toluene solution), with pure terpineol (0.01 cm.<sup>3</sup> of a 10 per cent. alcohol solution) as a frothing agent.



wetting values are defined not by the electrolytes, but by collector adsorption which, however, may vary widely under the influence of "modifying" electrolytes.\* In a number of cases the action of regulating electrolytes amounts to the formation of hydrophile, very slightly soluble films of new surface compounds (depressing agents), or to the hindrance of the formation of such films (activating agents).

### Summary.

Wetting and Flotation—Hysteresis of Contact Angle and Wetting Isotherms—Kinetics of Adhesion and Film Thinning—Role of the Electric Double Layer in Flotation.

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\* The significance of electrocapillary phenomena at solid, metallically conducting surfaces is well illustrated by the phenomena studied in the author's laboratory. These studies are concerned with the facilitation of the mechanical dispersion of solids (poly- and monocrystals) by the formation of adsorption and solvation layers in microcracks which develop in the predispersion zone.

Upon grinding pyrite (FeS<sub>2</sub>) with corundum (E. Wenström's data), an addition of 0.1 per cent. of NaCl to pure water increases the rate of dispersion by 25 per cent. at constant expenditure of mechanical work. Cathodic polarisation (1.6 v.) gives in addition a further increase of 17 per cent. in the rate of dispersion, and an equal anodic polarisation, an increase of 35 per cent. Such a method, as well as measurements of the plastic flow and rupture of metal monocrystals (cf. P. Rehinder and E. Wenström, *Bull. Acad. Sci. URSS, sér. phys.*, 1937, 4-5, 531, 548), permit one to study electrocapillary phenomena at solid surfaces.

# THE "AMPHOTERIC" DOUBLE LAYER AND THE DOUBLE IONIC EXCHANGE IN SOILS.

BY SANTE MATTSON AND LAMBERT WIKLANDER.

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The highly amphoteric soils, such as the brown and red earths, adsorb and exchange simultaneously large quantities of anions and cations at, or near, their equi-ionic point (the  $pH$  at which equivalent amounts of anions and cations are adsorbed<sup>1</sup>). Since it has been shown by Teräsvuori,<sup>2</sup> by Möller<sup>3</sup> and by Du Rietz<sup>4</sup> that the mass law, as expressed by the Donnan equilibrium, applies to the exchange of cations, we concluded that it ought to apply to the exchange of the anions as well, and that the valence effect ought to express itself, in such a double exchange, in a very singular and definite relationship which should serve as a further proof of the application of the theory. Because of the intimate relationship to the structure and composition of the double layer we shall here present some of the results obtained. (A more detailed account will be published in *Soil Science*.)

We are aware of the fact that an application of the Donnan equilibrium to amphoteric colloids is extremely complicated and we admit that it might seem difficult to understand how an amphoteric soil, which at the equi-ionic point binds large quantities of anions and cations, can possess an electrostatically attracted swarm of free ions of opposite sign of charge. Why do not these ions distribute themselves in pairs equally throughout the system, since the colloidal ions would compensate each other like amphoteric "Zwitterionen"? But the acidoid and basoid ions may be too far apart to exert any appreciable interionic attraction.<sup>5</sup> In this case these ions will attract the diffusible ions of opposite sign of charge and thus form an "amphoteric" ionic atmosphere, within which the anions and cations alternately dominate from point to point. The soil particle may also consist of a mosaic of acidoid and basoid clusters outside of which "clouds" of cations (over the acidoid areas) and anions (over the basoid areas) would gather. This would especially be the case in the more heterogenous, less intimate mixtures of acidoids and basoids.

Let us briefly consider the two extremes in structure of such amphoteric systems:

1. The system consists of a single aggregate of an acidoid gel and another, chemically equivalent, aggregate of a basoid. Both of the

<sup>1</sup> S. Mattson and L. Wiklander, *Annals Agr. College of Sweden*, 1937, 4, 169.

<sup>2</sup> A. Teräsvuori, 1930. *Über die Bodenazidität, mit besonderer Berücksichtigung des Elektrolytgehaltes der Bodenaufschlammungen*. Akademische Abhandlung, Helsinki (Valtion Maatalouskoet. Julkaisuja No. 29).

<sup>3</sup> J. Möller, 1935. *Studier over Ionbyttningsprocessen, med saerlig Henblik paa Agrikulturkemien*. Dissertation, Danmarks Tek. Højskole, Kopenhagen.

<sup>4</sup> C. Du Rietz, 1938. *Über das Ionenbindungsvermögen fester Stoffe*. 124 pages. Dissertation, Kgl. Tek. Högskolan, Stockholm.

<sup>5</sup> S. Mattson and N. Karlsson, *Annals Agr. College of Sweden*, 1938, 6, 109.

colloids exist in the free acidoid and basoid form (unsaturated with bases and acids respectively). The aggregates are not in contact but exist in the same medium. Each aggregate has its double layer with H ions in the outer layer of the acidoid and OH ions in the outer layer of the basoid but, being separate, they cannot mutually interact and "neutralise" each other. A neutral salt is added to the system. The H ions are displaced by the cations and the OH ions by the anions of the salt. Since the displaced H and OH ions unite to form  $H_2O$  the adsorption of the ions of the salt may, within certain limits, be practically complete. If the displacing power of the anions and cations be different there may be exchange acidity or exchange alkalinity.

2. Let the acidoid and basoid gel aggregates be mixed as far as this is physically and chemically possible and we shall get our other extreme in amphoteric structure. The acidoid and basoid will mutually interact and "neutralise" each other as far as their strength allows. Some of the acidoid and basoid ions will unite, whereas some of these ions will remain more or less separated and thus maintain the double layer which, however, will possess a mixed, amphoteric structure. The capacity of the system to adsorb and exchange ions will, of course, be reduced, the more so the greater the "neutralisation" and the closer the remaining free acidoid and basoid ions are to each other.

Between these extremes we may have every transition of mixtures.

Some of the diffusible ions may be evenly distributed in the interior of the gel while some of them form the external, diffuse Gouy layer.

The composition of the micellar solution must be according to the Donnan equilibrium, which for univalent ions is expressed by the equation: <sup>6, 7, 8.</sup>

$$x^2 = y(y + z) \quad \text{. . . . . (1)}$$

where  $x$  is the activity of the anions and cations of the free salt in the outside solution,  $y$  their activity in the micellar solution and  $z$  the activity of the ions dissociated by the colloid.

This equation demands that the product of the activities of any pair of ions must be the same at every place in the inside as in the outside solution. This means that where the cations are in excess (as over an acidoid ion or cluster of ions) there must be fewer anions than in the outside solution; *i.e.*, a positive adsorption of cations leads to a negative adsorption of anions and vice versa. That the result will, nevertheless, be an absolute adsorption by the amphoteric colloid of both anions and cations follows from the fact that the sum of the unequals is greater than the sum of the equals, *i.e.*,  $2y + z > 2x$ .

We shall, in what follows, assume that the amphoteric soil particle possesses, at and near the equi-ionic point, swarms of dissociated anions and cations. The ionic exchange must then take place according to the Donnan distribution of ions between the micellar (*i*) and the outside (*o*) solutions. The H ions of the acidoid will be displaced by the mono and divalent cations, *e.g.*, by Na and Ba ions, according to equation 2, and the OH ions of the basoid will be displaced by the mono and divalent anions, *e.g.*, by Cl and  $SO_4$  ions, according to equation 3 where the parenthesis indicates activity:

<sup>6</sup> J. Loeb, 1924. *Proteins and the theory of colloidal behaviour*, ed. 2. New York.

<sup>7</sup> S. Mattson, *Soil Sci.*, 1929, 28, 179.

<sup>8</sup> *Ibid.*, 1932, 33, 301.

$$\frac{(H^*)_i}{(H^*)_0} = \frac{(Na^*)_i}{(Na^*)_0} = \frac{\sqrt{(Ba^{**})_i}}{\sqrt{(Ba^{**})_0}} \quad (2)$$

$$\frac{(OH^*)_i}{(OH^*)_0} = \frac{(Cl')_i}{(Cl')_0} = \frac{\sqrt{(SO_4'')_i}}{\sqrt{(SO_4'')_0}} \quad (3)$$

In these equations the divalent ions enter as the square root of their activity. This means that a dilution, which affects the outside solution much more than the inside, will favour the entrance of the divalent and the exit of the monovalent ions. That is, the relative displacing power of the divalent ions will be greatly enhanced in dilute solutions, whereas at high concentrations the displacing power of the two ions should be more nearly balanced, provided that the different saloids are completely or equally dissociated. (The special position occupied by the H and OH ions must be ascribed to a limited dissociation of the acidoids and basoids.) From this we can draw the following consequences:

If to an unsaturated soil, whose acidoid and basoid groups are present in equivalent proportion, we add increasing concentrations of a neutral salt solution containing a divalent cation and a monovalent anion, *e.g.*,  $BaCl_2$ , we ought to get the following results:

In low concentrations the Ba ions will displace considerably more H ions than the Cl ions will displace OH ions. In higher concentrations the two reactions will more nearly balance each other. The exchange acidity must therefore attain a maximum in dilute solutions and then decrease in higher concentrations.<sup>9</sup>

If we add a solution containing a divalent anion and a monovalent cation, *e.g.*,  $Na_2SO_4$ , we ought to get a maximum exchange alkalinity in dilute solution.

To test this theory we selected a sample from the B horizon of an iron podzol (from Furudal, Dalarna), which had the same pH in water and in N/100 NaCl solution. We took this as an indication of an equivalence between the acidoid and basoid groups. The pH was determined by the glass electrode in water and in various concentrations of  $Na_2SO_4$  up to 2 N. The results, given in Fig. 1, show that a N./50 solution yielded a maximum in exchange alkalinity equal to 0.52 pH unit, whereas a 100 times stronger solution yielded only a 0.24 unit higher pH than in water.

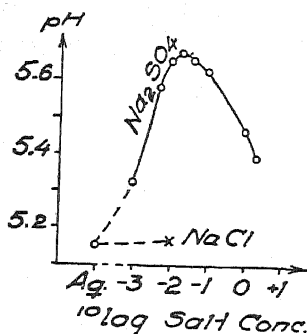


FIG. 1.—The pH of the Furudal soil in water and in solutions of various concentrations of  $Na_2SO_4$ .

(lateritic surface soil and iron podzol samples from the B-horizon). An excess of acidoids over basoids always resulted in an exchange acidity in both salt solutions (humus soils and gray soils). A little reflection will show that this is all in agreement with the theory. The relationship is,

<sup>9</sup> A disturbing factor, especially when the acidoid content is high and the exchange acidity great, will be the dissolution of the basoid-bound Cl ions in the form of  $AlCl_3$  which by hydrolysis gives HCl.

however, very complicated, because the position and magnitude of the maxima in exchange alkalinity and exchange acidity are governed by several factors, *viz.*, by the valence, by the concentration ( $z$ ) in the micellar solution of the ions "belonging" to the colloid, by the concentration of the colloid and by the ratio of acidoids to basoids. Before we present any more of the experimental data we shall, therefore, profit by constructing a few theoretical curves which illustrate the influence of these factors.

Knowing neither the activities nor the concentrations of the ions in the micellar solution and knowing of no reliable method by which these may be calculated in so complex systems as soils we shall confine ourselves to a qualitative application of the above equations on the basis of certain assumptions.

The influence of the concentration of the colloid and of the value of  $z$  is brought out in Table I and in Fig. 2. The calculated concentrations are approximations in so far that we have put the inside concentration equal to a constant ( $= z$ ) and ignored the concentration of the free electrolyte ( $= y$  in equation 1). This does not involve any serious error so long as the latter is small compared with  $z$ , but where the outside concentration approaches that of the inside as in Table I (IIa) and Fig. 2 the results become misleading. With this exception the results are sufficiently accurate to bring out the true relationship.

The calculations apply to an unsaturated amphoteric soil whose acidoid/basoid ratio  $= 1$  and which is assumed to be present in the concentrations of 100, 10 and 1 milliequivalents per litre, the value of  $z$  being in one case (I) put equal to  $N/1$  and in the other (II) to  $N/10$ .

The assumption of a complete dissociation of the acidoid and basoid as well as of their salts makes the concentration of the displaced H and OH ions very large. But this need not disturb us, for we are here not concerned with the true concentrations of the displaced H and OH ions but with the relative proportions of the displaced ions.

Table I and Fig. 2 show that the maxima  $m$  in exchange acidity and exchange alkalinity must occur at a lower concentration of the salt, (1) the lower the concentration of the soil suspension (or the lower the colloid content of the soil) and (2) the higher the concentration  $z$  of the ions dissociated by the colloid (II a omitted).

The maxima in Fig. 2 occur approximately at the following concentrations of the salts  $M^+S^-$  and  $M^{++}S'^-_2$ :

Acidoid = basoid =	100.	10.	1 m. equiv./l.
$z = N/1$ . .	0.008	0.00045	0.000025
$z = N/10$ . .	—	.0009	.00005

These positions of the maxima, especially those at the higher concentrations, are somewhat lower than the true theoretical positions, due to the use of  $z$  instead of  $y + z$ .

The two maxima in each pair of curves in Fig. 2 occur at the same concentration of salt because in each system we are assuming an equivalence between acidoids and basoids and assign the same value for  $z$  to both groups. In the soil we might have any proportion between these factors and the maxima in exchange acidity and exchange alkalinity may, therefore, occur at different concentrations of the salts. If, for



example, the basoid content of a system be decreased, or the acidoid content increased, then the maximum in exchange acidity will not only become greater but must also be deflected to a higher salt concentration, whereas the maximum in exchange alkalinity will become smaller and occur at a lower concentration of salt. If, on the other hand, the acidoid

TABLE I.—THE APPROXIMATE THEORETICAL DISPLACEMENT OF H AND OH IONS AT VARIOUS CONCENTRATIONS OF AN UNSATURATED SOIL (ACIDOID = BASOID = (a) 100, (b) 10 AND (c) 1 M.EQUIV. PER LITRE) BY NEUTRAL SALTS OF THE TYPE  $M^+S'^-$  AND  $M^+S''^-$ , WHEN THE CONCENTRATION ( $z$ ) OF THE IONS DISSOCIATED BY THE COLLOID IS (I)  $N/1$  AND (II)  $N/10$ . (Cf. formulæ 2 and 3, and Fig. 2.)

Conc. in the Inside Solution.		Concentration in the Outside Solution.		
H <sup>+</sup> or OH <sup>-</sup> .	M <sup>+</sup> or M <sup>++</sup> S' or S''.	H <sup>+</sup> or OH <sup>-</sup> .	M <sup>+</sup> or S'.	M <sup>++</sup> or S''.
(Ia) = 100 m. equiv./l., $z = N/1$ .				
0.9	0.1	0.01	0.0011	$1.23 \times 10^{-5}$
.8	.2	.02	.0050	$1.25 \times 10^{-4}$
.6	.4	.04	.0266	0.00178
.5	.5	.05	.0500	.005
.4	.6	.06	.0900	.0135
.2	.8	.08	.3200	.128
.1	.9	.09	.8100	.729
(Ib) = 10 m. equiv./l., $z = N/1$ .				
0.9	0.1	0.001	0.00011	$1.23 \times 10^{-7}$
.8	.2	.002	.00050	$1.25 \times 10^{-6}$
etc.	—	—	—	—
(Ic) = 1 m. equiv./l., $z = N/1$ .				
0.9	0.1	0.0001	0.000011	$1.23 \times 10^{-9}$
.8	.2	.0002	.000050	$1.25 \times 10^{-8}$
etc.	—	—	—	—
(IIa) = 100 m. equiv./l., $z = N/10$ .				
0.09	0.01	0.01	0.0011	$1.23 \times 10^{-4}$
.08	.02	.02	.0050	$1.25 \times 10^{-3}$
etc.	—	—	—	—
(IIb) = 10 m. equiv./l., $z = N/10$ .				
0.09	0.01	0.001	0.00011	$1.23 \times 10^{-6}$
.08	.02	.002	.00050	$1.25 \times 10^{-5}$
etc.	—	—	—	—
(IIc) = 1 m. equiv./l., $z = N/10$ .				
0.09	0.01	0.0001	0.000011	$1.23 \times 10^{-8}$
.08	.02	.0002	.000050	$1.25 \times 10^{-7}$
etc.	—	—	—	—

content of the system be decreased, or the basoid content increased, then the effect will be the opposite.

This is illustrated in Fig. 3. The calculations apply to unsaturated soil suspensions whose acidoid/basoid ratios vary between 5.0 and 0.2 and whose acidoid and basoid concentrations are put at 2 to 10 milli-

equivalents per litre, the value of  $z$  being assumed to be equal to  $N/1$  in every case.

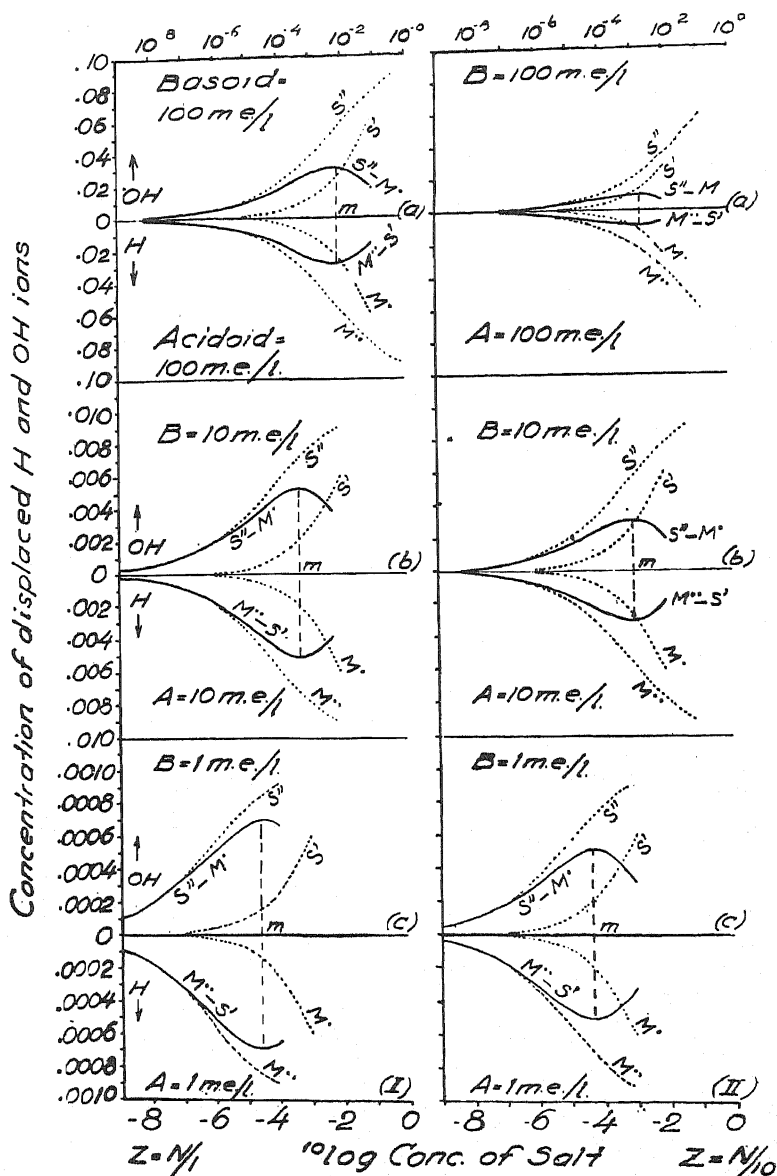


FIG. 2.—The maxima in exchange alkalinity and exchange acidity in solutions of salts of the types  $M' \cdot S''$  and  $M'' \cdot S'$ , as related to the concentration of colloid (a, b, and c) and to the concentration  $z$  of the ions dissociated by the colloid (I and II) as based on Table I.

If we compare the curves in Fig. 3 with the curves in 1b in Fig. 2 we note that a decrease in basoids (= increase in acidoid/basoid ratio) causes the maximum in exchange alkalinity ( $m'$ ) to be smaller and to be deflected toward a lower salt concentration, whereas the maximum

in exchange acidity ( $m'$ ) becomes larger and is deflected toward a higher concentration of salt. (Cf. curves in Fig. 3 (a) and (b).) A decrease in acidoids (= decrease in acidoid/basoid ratio) has the opposite effect. (Cf. curves in Fig. 3 (c) and (d).)

The maxima in exchange alkalinity in solution  $M^*S''$  and in exchange acidity in solution  $M^*S'_2$  occur, in the different proportions of acidoid

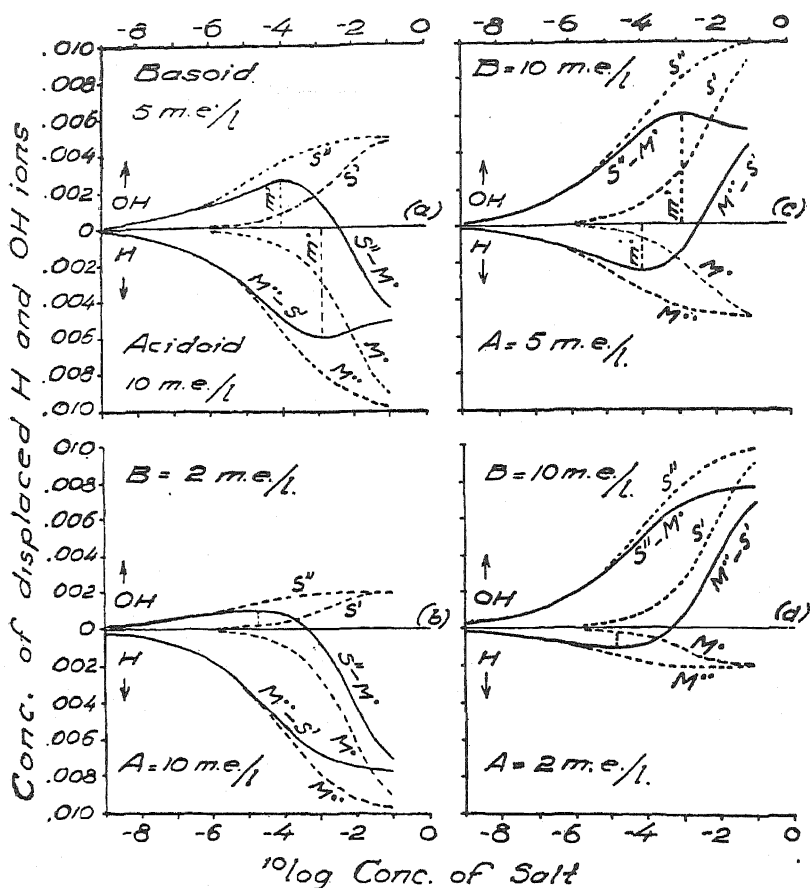


FIG. 3.—The maxima in exchange alkalinity and exchange acidity as related to the acidoid/basoid ratio.

to basoid, approximately at the following equilibrium concentrations of the salts:

Fig.	3(b).	3(a).	2 I(b).	3(c).	3(d).
Acidoid m.equiv./l.	10	10	10	5	2
Basoid m.equiv./l.	2	5	10	10	10
$M^*S''$ n	0.000016	0.00010	0.00045	0.00135	$\infty$
$M^*S'_2$ n	$\infty$	0.00135	0.00045	0.0010	0.000016

We shall now present our experimental data and show how we have applied the principles to a study of soil profiles.

### Experimental.

For a study of the application of the principles here developed we selected (among other materials not here discussed) a subsoil (sample IV)

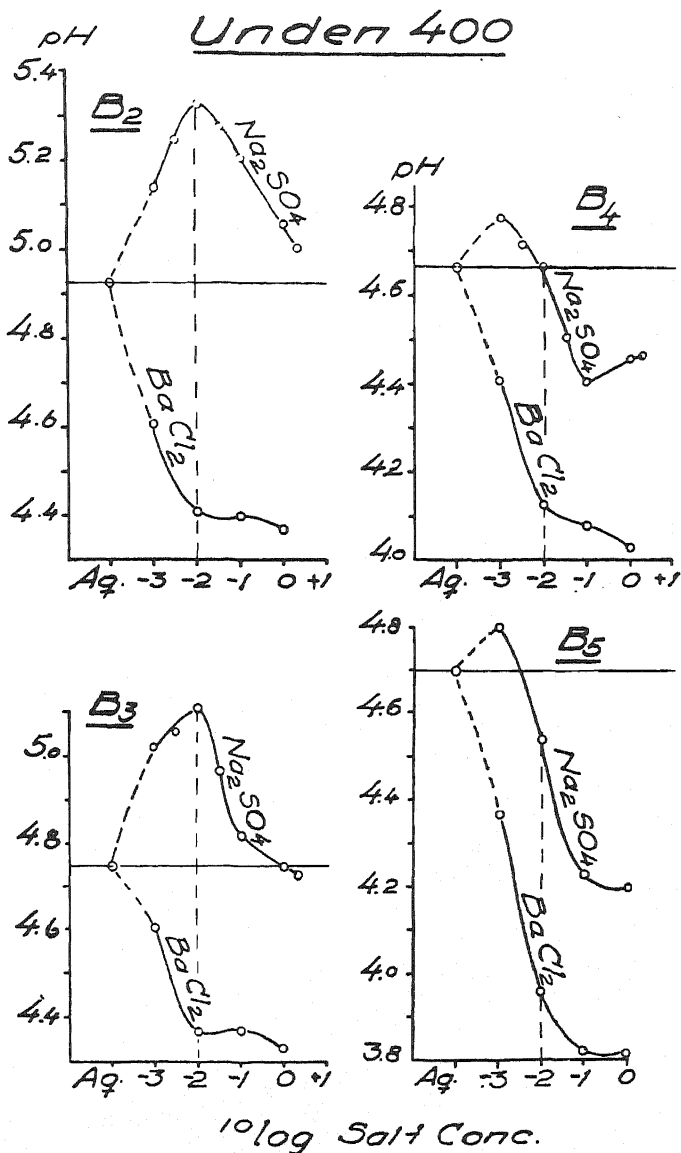


FIG. 4.—The maxima in exchange alkalinity and exchange acidity in the B horizons of the Unden profile 400.

from the Las Mesas laterite, Mayaguez, Puerto Rico, and seven samples from the B horizons of the Unden series of podzol profiles from

Västergötland in Sweden.<sup>10</sup> These materials are practically unsaturated with cations and anions in their natural condition.

Fig. 4 gives the pH in water and in various concentrations of  $\text{BaCl}_2$  and  $\text{Na}_2\text{SO}_4$  of a vertical series of four of the Unden podzol samples (profile 400, horizons  $B_2$  to  $B_3$ ).

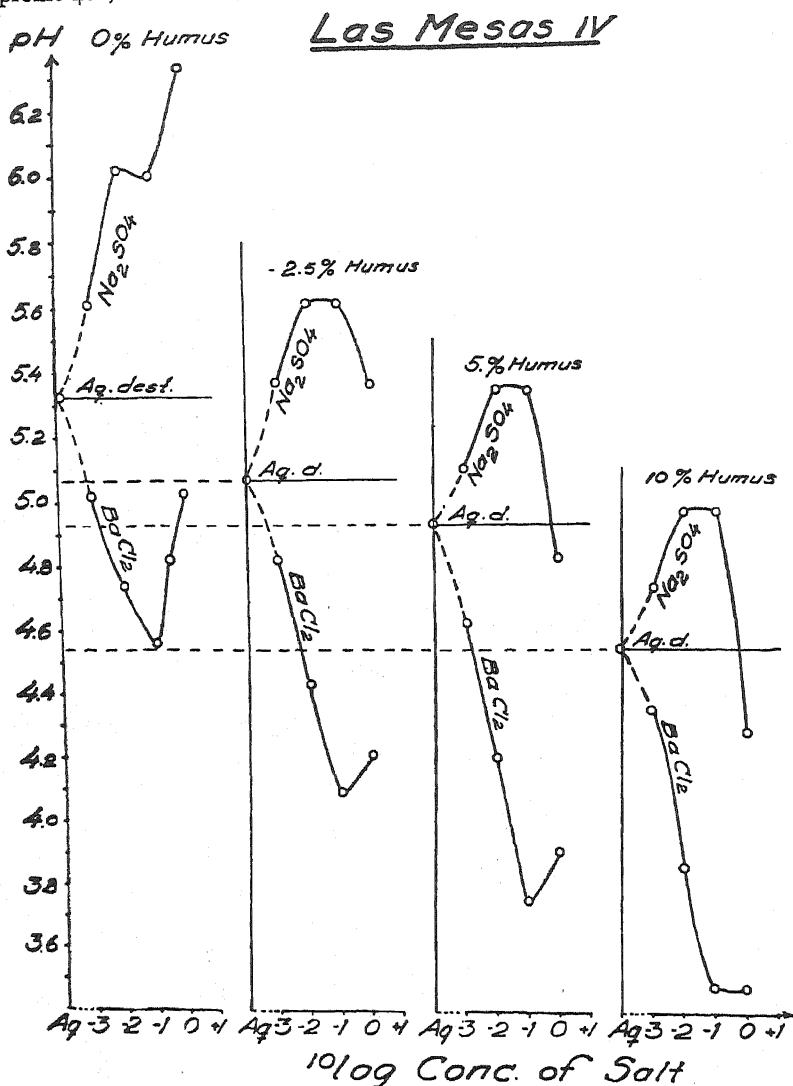


FIG. 5.—The influence of humus on the exchange reactions of the Las Mesas laterite subsoil.

The following facts are of interest in connection with the theory :

1. The exchange alkalinity in  $\text{Na}_2\text{SO}_4$ , which is greatest in  $B_2$ , decreases with an increase in exchange acidity in  $\text{BaCl}_2$ , which is greatest in  $B_1$ .

<sup>10</sup> The Unden profile series is a hydrologic series covering all transitions in wetness and dryness.<sup>11</sup>

<sup>11</sup> S. Mattson and H. Lönnemark, *Annals Agr. College of Sweden*, 1939, 7, 185.

2. As the exchange alkalinity is decreased its maximum is deflected toward a lower concentration of salt (from an initial concentration of about  $N./100$  in  $B_2$  to  $N./1000$ , or less, in  $B_3$ ). At the same time the maximum in exchange acidity is deflected towards a higher concentration of salt.

This is in agreement with the theory as illustrated in Fig. 2 (b) and Fig. 3 (a) and (b). It is obvious that when the acidoids greatly exceed the basoids the exchange alkalinity must reach a vanishing point (at very low concentration of salt) and that the exchange acidity must assume a maximum in the most concentrated solution exactly as shown in the figures.

The decrease in exchange acidity of  $B_4$  in  $Na_2SO_4$  above  $N./10$  we are unable to explain unless it can be ascribed to abnormal changes in the activity coefficients of the various ions at high concentrations in the inside solution. (An abnormal decrease in the activity coefficient of the  $SO_4$  ions or an increase of that of the  $Na$  ions in the inside solution would account for the phenomenon.)

**The Influence of Humus.**—The stronger acidoid properties observed in the Las Mesas surface soil than in the subsoil could primarily be ascribed to humus acidoids. A systematic study of the influence of humus upon the reactions of the laterite was made by adding 2.5, 5.0 and, 10.0 % of humus acidoid (obtained by extracting peat with  $NaOH$  precipitating with  $H_2SO_4$ , and electrolysing the precipitate until free from acid) to the Las Mesas IV and then determining the  $pH$  in water and in increasing concentrations of  $Na_2SO_4$  and  $BaCl_2$ . The results are shown in Fig. 5.

Compared with the sample to which no humus was added we note the following :

1. The  $pH$  in water is lowered by the humus.
2. The exchange alkalinity in  $Na_2SO_4$  is reduced and this reduction is much greater in the concentrated ( $N./1$ ) solution, which yields an

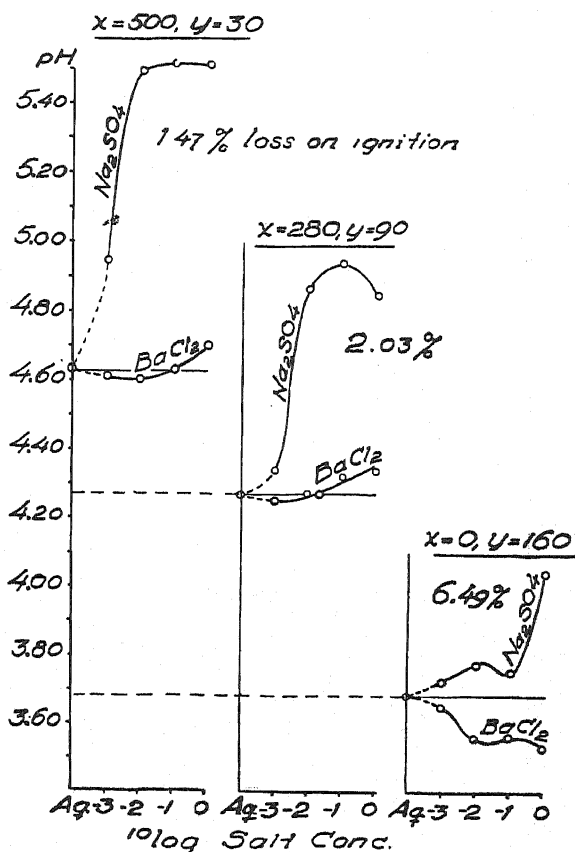


FIG. 6.—The exchange reactions of the most basoid samples (cf. Fig. 8) from three of the Unden profiles.

exchange acidity with 5 and 10 per cent. humus. This gives rise to pronounced maxima in exchange alkalinity in the dilute solutions (between N./100 and N./10 initial concentration).

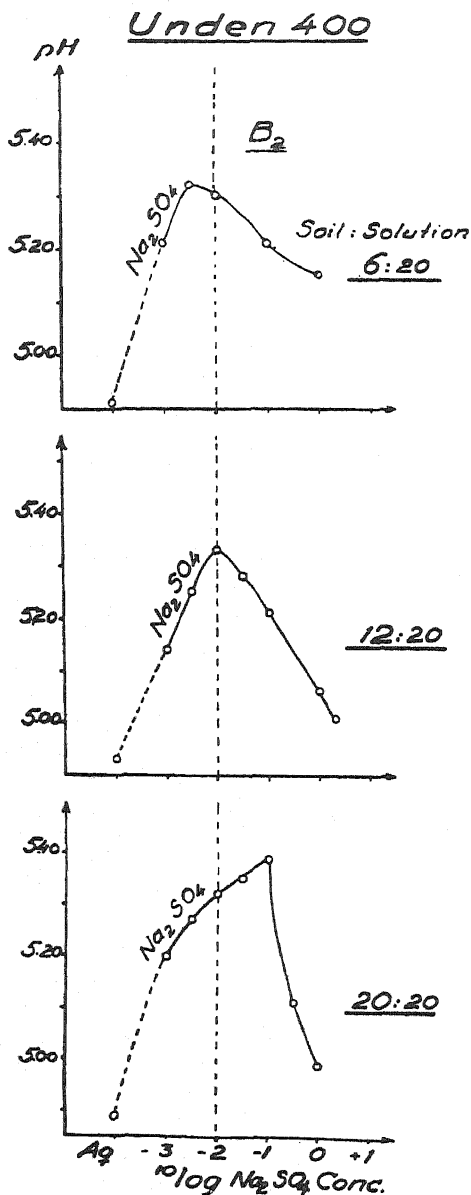


FIG. 7.—The influence of the concentration of the soil suspension on the maximum in exchange alkalinity.

3. The exchange acidity in  $\text{BaCl}_2$  is increased and this increase is greater in the concentrated solution (N./1) so that the maxima in the dilute solutions (about N./10) become less pronounced and finally vanish (with 10 % humus).

This all agrees, in a general way, with the theory as outlined in Fig. 3. We have reasons to believe that the exchange acidities in the stronger  $\text{BaCl}_2$  solutions would be smaller were it not for the presence of small amounts of  $\text{SO}_4$  ions in the laterite and for the hydrolysis of aluminium and ferric chlorides.

Besides the vertical series from the B horizons of the Unden podzol profile 400 we have selected a horizontal series by taking the most strongly basoid sample (cf. Fig. 8) from three of the Unden series of profiles.

Fig. 6 gives the pH in water and in different concentrations of  $\text{Na}_2\text{SO}_4$  and  $\text{BaCl}_2$ . Sample  $x = 500$  ( $y = 30$ ) \* comes from the dry end of the profile series and is the most strongly basoid of all. With a loss on ignition of only 1.47 % this sample yields an exchange alkalinity with all but the dilute solutions of  $\text{BaCl}_2$ . The nearest theoretical counterpart is found in Fig. 3 (d).

Sample  $x = 280$  ( $y = 90$ ), with its 2.03 % loss on ignition is somewhat less strongly basoid, but even this sample yields a slight exchange alkalinity in N./1  $\text{BaCl}_2$ . The nearest theoretical counterpart is found in Fig. 3 (c).

Sample  $x = 0$  ( $y = 160$ ) with 6.49 % loss on ignition yields curves which seem difficult to interpret.

\*  $x$  and  $y$  refer to co-ordinate values where  $x$  = horizontal and  $y$  = vertical distance from a point of origin on the surface of the ground at the dry end of the series.

It should be pointed out that this sample comes from the wet end of the profile series and represents apparently gleyed material. The low  $pH$  might be another factor. The sample possesses apparently a fairly strong basoid group in spite of the high humus content but before the samples have been analysed it is impossible to say what specific influence may be present.<sup>11</sup>

**The Influence of the Concentration of the Colloid.**—Having shown how variations in the acidoid/basoid activity ratio affect the maxima in exchange acidity and exchange alkalinity it remains to show how variations in the concentration of the colloid affect these maxima when the acidoid/basoid ratio remains the same.

According to Fig. 2 an increase in concentration should deflect the maxima towards a higher concentration of salt. Fig. 7 shows the exchange alkalinities in various concentration of  $Na_2SO_4$  of the B<sub>2</sub> sample of the Unden profile 400 in the proportions of 6, 12 and 20 grams of soil to 20 c.c. solution.

The curves show that an increase in the concentration of the soil result in (1) an increase in exchange alkalinity and (2) a deflection of the maximum toward a higher concentration of salt.

Even these results are in general agreement with the theory and yield information which, if it could be quantitatively interpreted, would be of very great importance, for we should then be able to determine the quantity of colloid in a soil merely by means of a few simple  $pH$  determinations. But even the qualitative results which the method yields will lend themselves to important applications.

### Application to Soil Profiles.

Having established the factors which govern the amphoteric reactions of soils we are in a position to reciprocate and by means of these reactions, *i.e.*, the  $pH$ , determine, qualitatively and, in a comparative sense, quantitatively, these factors.

We are here presenting the results of the application of the method to three of the Unden profiles and to the Las Mesas laterite.

Fig. 8 gives the difference between the  $pH$  of the soil in water and its  $pH$  in  $N./100$   $Na_2SO_4$  and  $BaCl_2$  solutions at different depths of the profiles. These differences express the exchange acidity (positive values) and exchange alkalinity (negative values) of the soil materials.

Since the samples have not yet been analysed it is too early to attempt a detailed discussion of the results. In the case of the podzol profiles we shall here merely call the reader's attention to the maximum in exchange alkalinity in the upper B horizon. This maximum expresses a high basoid activity resulting from the isoelectric precipitation of the cationic sol complex which has come from the A horizon. Then there is another maximum in the gley horizon (G) due to an accumulation of ferric hydroxide formed by the oxidation of soluble ferrous compounds.

This method which is based upon a determination of the *activities* of the acidoid and basoid groups (as distinguished from the analytical determination of the *quantities* of acidoid and basoid materials) offers a simple, direct and scientific expression for the podzolisation of a soil.<sup>12</sup>

The samples of the laterite used in this experiment were electro-dialysed to remove the displaceable  $SO_4$  ions which were present in small but considerable amounts in the II, III and IV samples.

The differences between the  $pH$  values in water and in the  $N./1$  and  $N./100$  salt solutions are shown in Fig. 8. We get here a different picture from that of the podzol profiles. The characteristic maxima and minima in the podzols are absent in the laterite. The exchange alkalinity of the laterite in the sulphate solutions is lowest in the surface soil and attains

<sup>12</sup> For a complete report on the work of the Unden series *cf.* <sup>11</sup>.



a uniform high value in all the subsoil samples. The exchange acidity in  $\text{BaCl}_2$  ought to be greater in sample I than in the three subsoil samples. The fact that this is not the case must be ascribed to the  $\text{SO}_4$  ions which,

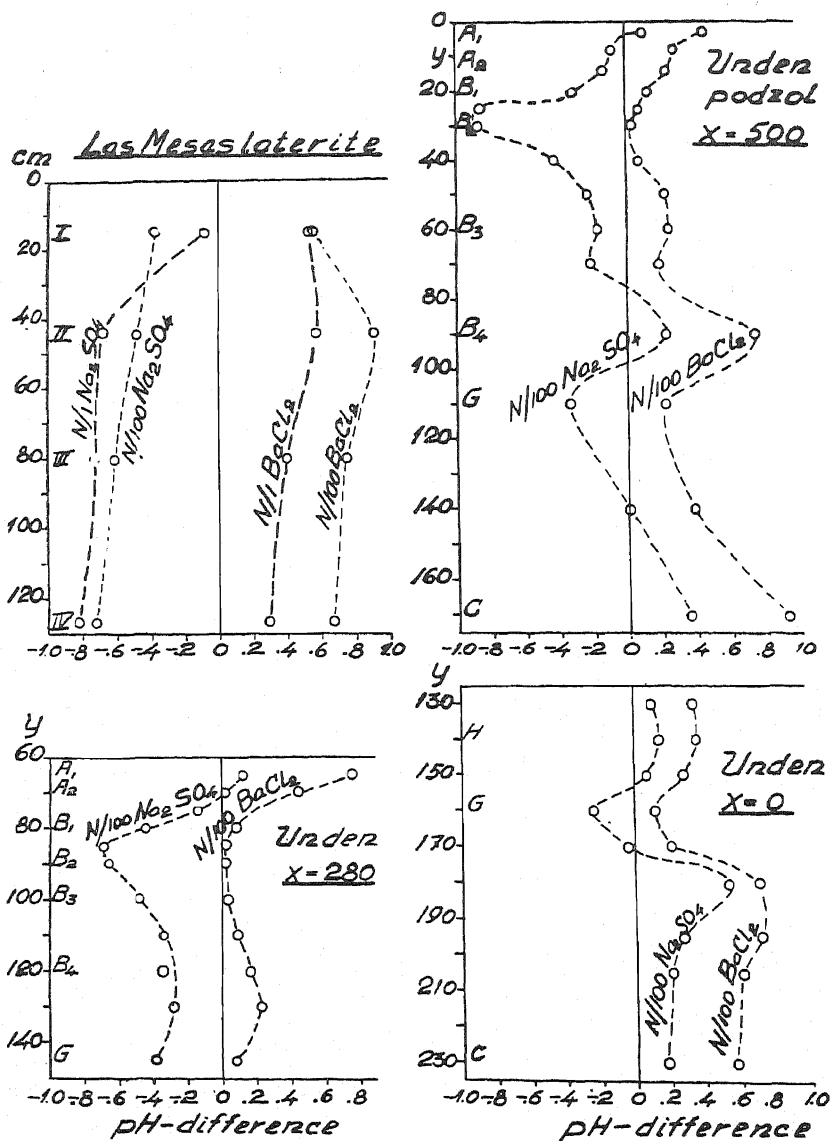


FIG. 8.—The differences between the  $\text{pH}$  in water and in the salt solutions in various depths of the Las Mesas laterite and in three of the Unden podzol profiles. Negative values = exchange alkalinity. Positive values = exchange acidity.

in spite of a prolonged electrodialysis (one week), still remained in samples II, III and IV as was shown by extracting the soil with a hot ammoniacal solution of  $\text{NH}_4\text{Cl}$ . Since these subsoil samples yielded a still greater exchange acidity before being electrodialysed we conclude that the

exchange acidities of these samples are still "abnormally" high whereas the exchange acidity of sample I more nearly expresses the true amphoteric nature of the soil complex.

Another significant thing in Fig. 8 (*cf.* Las Mesas) is the fact that the exchange alkalinity is greater in N./1 than in N./100  $\text{NaSO}_4$  and that the exchange acidity is greater in N./100 than in N./1  $\text{BaCl}_2$  in samples II, III and VI. This tells us that the basoid groups are very strong in these samples; so strong that (1) the effect of the  $\text{SO}_4$  ions *remains* stronger than that of the Na ions even in high concentrations and that (2) the effect of the Cl ions *becomes*, in high concentrations, greater than that of the Ba ions. In sample I the acidoid group is sufficiently strong to make the effect of the Na ions outweigh that of the  $\text{SO}_4$  ions in high concentrations. The same tendency is shown with respect to the Ba and Cl ions.

### Other Applications.

It has been pointed out that theoretically it would be possible to remove practically all the anions and cations from a solution by passing it through alternate layers, or a coarse mixture, of acidoids and basoids. In order to find out to what extent this is possible in the case of soil acidoids and basoids we performed the following experiment:

Twenty grams of electrolysed raw humus and 50 g. of Las Mesas II were separately moistened (to prevent intimate mixing and mutual interaction) with N./100  $\text{CaSO}_4$  and then lightly mixed and placed in a tall, sintered glass funnel. The mixture was then leached with the  $\text{CaSO}_4$  solution with the result that neither the first, second, third or fourth 50 c.c. of the filtrate showed any trace of Ca or  $\text{SO}_4$  ions.

The Donnan distribution of ions in the soil has many other important consequences. Consider, for example, the effect of a concentration and a dilution of the soil solution on the mobility of the mono and divalent ions. A dilution favours the entrance (in the soil complex) of the divalent and the exit (in the soil solution) of the monovalent ions. A concentration reverses the process. One might say that the soil complex "inhales" divalent and "exhales" monovalent ions upon wetting and "inhales" monovalent and "exhales" divalent upon drying. Since a leached soil means a dilute soil solution we can readily understand why, in the humid soils, the divalent base forming cations are present in the exchange complex in a greater proportion than in the original silicate rocks and in the soil solution.

### Summary.

The simultaneous exchange of anions and cations at the equi-ionic point of soils takes place according to the mass law as expressed by the Donnan equilibrium. The valence effect expresses itself in the form of maxima in exchange acidity and exchange alkalinity in dilute solutions.

The double ionic exchange has led to the conception of an amphoteric electrical double layer.

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## ERRATA.

Page 55, Table I. The molar concentration of  $\text{BaCl}_2$  in the fourth line should be 0.00025 and not 0.00025.

Owing to war conditions Professor Kruyt's corrections have only just been received. The following are the most important:—

Page 110, Para. 3, line 6. For "*in sufficiently*" read "*insufficiently*."

„ 111. The asterisk below equation 1 should attach to the last sentence of the paragraph, at the first mention of "*ions*."

Equation (un-numbered) above eqn. 1. For "*z*," read "*z<sub>1</sub>*."

Para. 3, line 3. For "*reserve*" read "*reverse*."

Para. 4, second equation. For "*χ*" read "*κ*."

„ 112. At foot of page. Capacities should be expressed in *capital* italics.

Footnote 1. For "*one voltage*" read "*over-voltage*."

„ 113. Equation (1). For "*d<sub>1</sub>*" read "*a<sub>1</sub>*."

Equations 1 and 2. For "*Z<sub>1</sub>*" read "*z<sub>1</sub>*."

Eleven lines below Fig. 2. After "*completely*" insert "(value of  $\epsilon = \epsilon_0$ )."

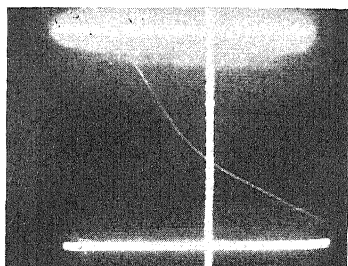
„ 114. In first three equations. For "*Z<sub>1</sub>*" read "*z<sub>1</sub>*."

Six lines below equation (4). For "*a<sub>v</sub>*" read "*a<sub>1</sub>*."

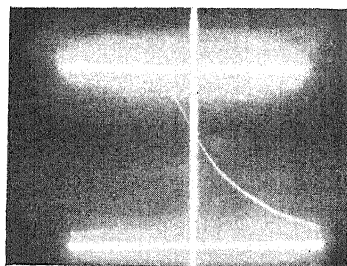
„ 116. For last sentence read: "*From the calculations of Hamaker and Levine it has become clear that, although  $\zeta$  is an important factor in the stability of colloids it is not the only determining one, and that other quantities (size of the particles, concentration of the solution, van der Waals' attraction) have to be taken into account. These calculations, however, are so very complicated, that the problem is still far from being solved, and it is no wonder that other theories have been put forward. We mention here only the theory of Ostwald, who explains the stability of colloids as a property of the solution, the 'activity coefficient' being the determining factor.*"

"*The intricacy of this question is most clearly demonstrated by realising that after more than 30 years of strenuous research we only just begin to see our way through this most fundamental problem of the chemistry of colloids.*"

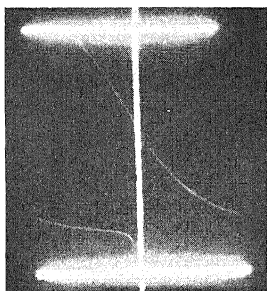
PLATE 1.



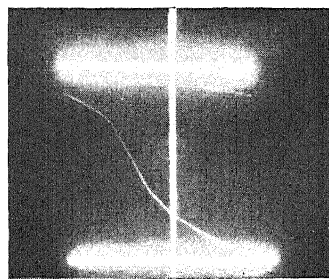
(a)



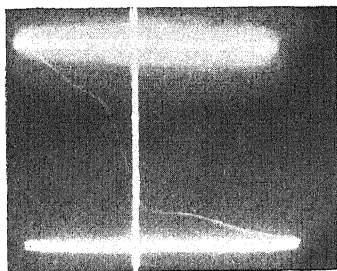
(b)



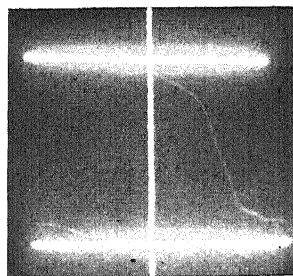
(c)



(d)



(e)



(f)

FIG. 2.—Typical Oscillograms.

- (a) N. Sulphuric acid ;  $F = 150$ ,  $i = 1.88 \times 10^{-2}$  amp.  
 (b) N. Hydrochloric acid ;  $F = 150$ ,  $i = 1.80 \times 10^{-2}$  amp.  
 (c)  $\frac{N}{100}$  Hydrochloric acid ;  $F = 200$ ,  $i = 1.65 \times 10^{-2}$  amp.  
 (d) N. Hydrochloric acid with tetraethylammonium chloride ( $M/10$ ) ;  
 $F = 250$ ,  $i = 2.90 \times 10^{-2}$  amp.  
 (e) N. Hydrochloric acid with *t*-amyl alcohol ( $M = 115 \times 10^{-3}$ ) ;  
 $F = 150$ ,  $i = 1.70 \times 10^{-2}$  amp.  
 (f) N. Hydrochloric acid with *t*-amyl alcohol ( $M = 271 \times 10^{-3}$ ) ;  
 OLD SURFACE,  $F = 150$ ,  $i = 1.70 \times 10^{-2}$  amp.  
 ( $F$  = sweep frequency.)

[See page 130.

PLATE 11.

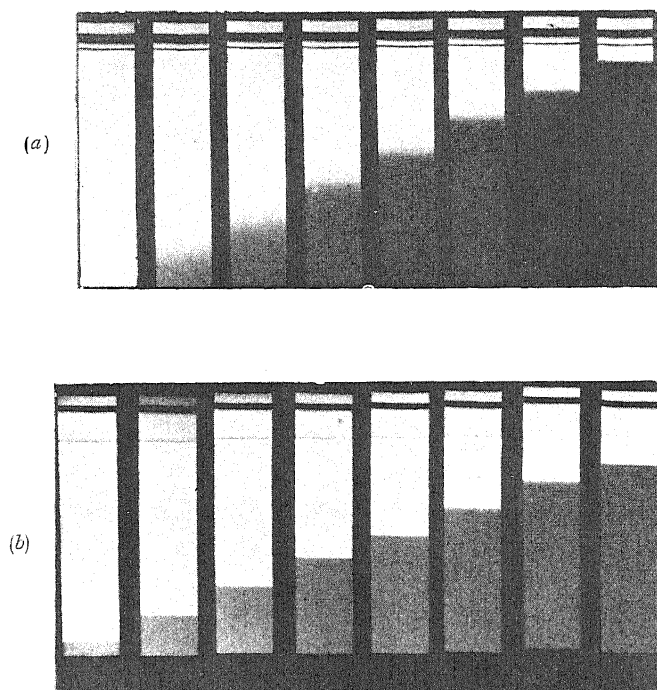


FIG. 1.—Sedimentation photographs of (a) vaccinia virus. Centrifugal force 850 xg. Photographs at 8-minute intervals by U-V absorption method, and (b) Bushy stunt virus. Centrifugal force 20,000 xg. Photographs every 9 minutes. (McFarlane and Kekwick, 1938).

[See page 257.

PLATE III.

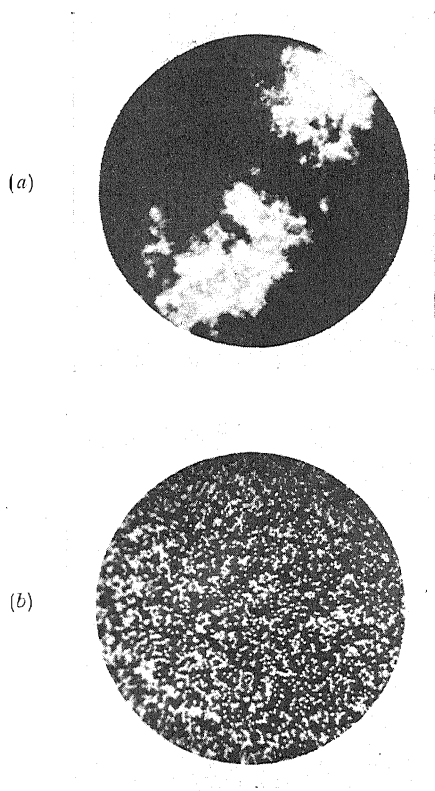


FIG. 2.—Photomicrographs by Dr. C. R. Amies of vaccinia, (a) flocculated, and (b) after resuspension by grinding. Dark-ground illumination.

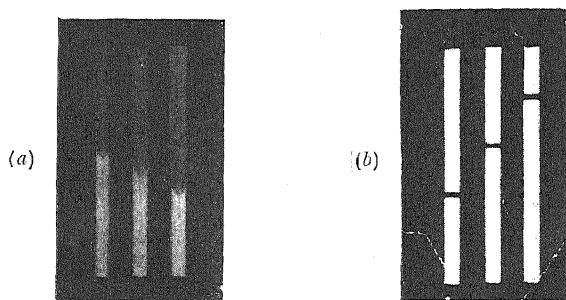
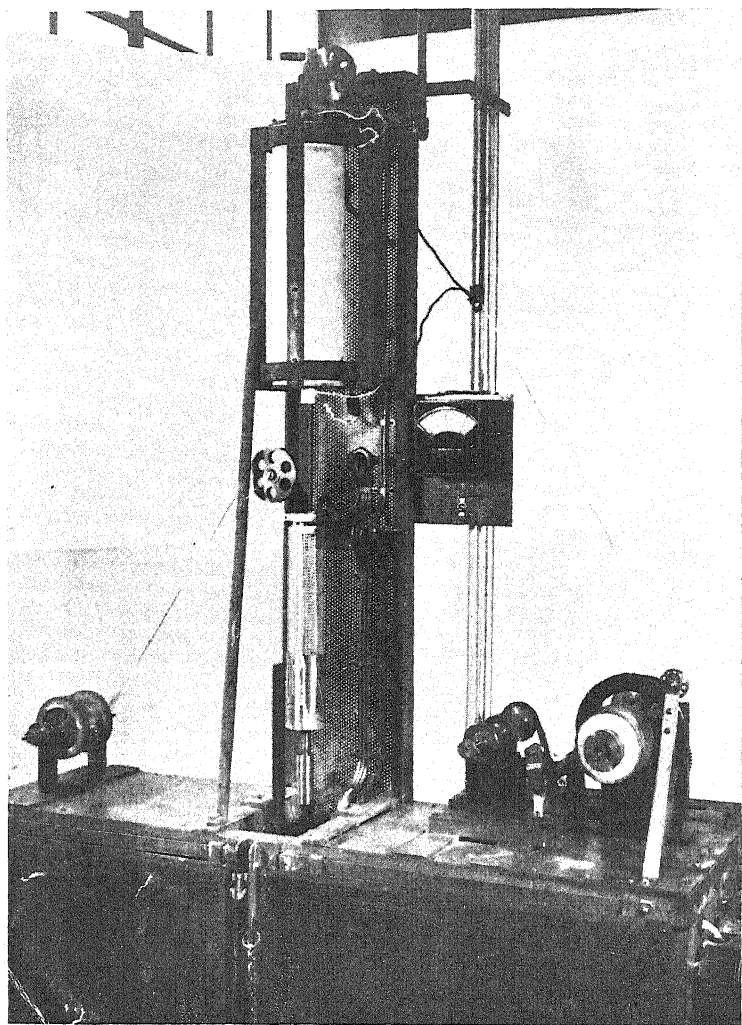


FIG. 3.—Electrophoresis in Tiselius apparatus of (a) vaccinia virus. Note endosmotic stream in centre of tube. Photograph by light absorption; and (b) Bushy stunt virus. Photograph by Toepler "Schlieren" method.

[See page 260.



PLATE IV.



Apparatus for coating Wires and Strips.

[See page 288.]

11 MAR. 1940

# OPTICAL SENSITISATION AND ADSORPTION OF DYES ON SILVER HALIDE: THE STATE OF THE ADSORBED DYE.\*

By E. P. DAVEY.

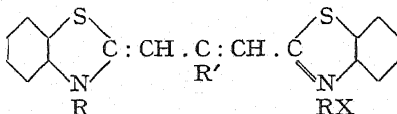
Received in original form 20th July, 1939, and as amended  
17th November, 1939.

Recently a considerable advance has been made in the study of the theory of the optical sensitisation of silver halide by dyes. In particular papers by Leermakers, Carroll and Staud,<sup>1, 2, 3</sup> by Sheppard, Lambert and Walker,<sup>4</sup> by Sheppard,<sup>5</sup> are of great interest, and will be referred to often in this study.

## Experimental.

The adsorbing medium was a photographic silver bromide emulsion containing about 3 % of silver iodide, of moderate speed, and chosen because it responded well to optical sensitisation. 5 c.c. of methyl alcohol containing the required amount of dye was added from a pipette to 50 c.c. of emulsion, with stirring, at 45° C., and left at this temperature for half an hour with stirring. 25 c.c. of this sensitised emulsion was diluted to 100 c.c. with warm water and centrifuged. The dilution of the emulsion introduced no error under the conditions of experiment, since no dye was found to redissolve during centrifuging. The dye was extracted from the halide by taking the latter up in 100 c.c. of water, fixing out with 50 c.c. of 40 % sodium thiosulphate, and extracting with 50 c.c. of *n*-butyl alcohol. In the presence of the thiosulphate, extraction was very nearly complete. The alcohol layer was separated, made up to 50 c.c. (necessary because of the partial mutual solubility between butyl alcohol and water), and the dye was estimated colorimetrically. For alcohol solutions, Beer's Law holds.

Certain sensitising cyanine dyes were used. The numbering adopted here corresponds, as far as possible, to that used by Leermakers *et al.* Dyes II, IV and VIII were thiacyanine dyes of the general formula:



\* Communication No. H740 from the Kodak Research Laboratory, Wellesley, Harrow, Middlesex.

<sup>1</sup> J. A. Leermakers, B. H. Carroll, and C. J. Staud, *J. Chem. Physics*, 1937, **5**, 878.

<sup>2</sup> J. A. Leermakers, *ibid.*, 889.

<sup>3</sup> J. A. Leermakers, B. H. Carroll, and C. J. Staud, *ibid.*, 893.

<sup>4</sup> S. E. Sheppard, R. H. Lambert, and R. D. Walker, *ibid.*, 1939, **7**, 265.

<sup>5</sup> S. E. Sheppard, *Optical Sensitising of the Silver Halides*, 8th Congress of Chemistry, Rome, 1938, **1**, 234-283.

in which R is an alkyl group, R' is alkyl or hydrogen, and X is a halide ion. Dye IX was similar, but benzselenazole rings replaced the benzthiazole. Dye VII was pinacyanol, having two quinoline rings, and dye V a cyanine, with only one methine group in the conjugate chain. Details are as follows:—

Dye II.	2 : 2'-dimethyl-8-ethylthiacarbocyanine bromide.
Dye IV.	8-methyl-2 : 2'-diethylthiacarbocyanine bromide.
Dye V.	1 : 1'-diethyl-2 : 2'-cyanine iodide.
Dye VII.	1 : 1'-diethyl-2 : 2'-carbocyanine iodide.
Dye VIII.	5 : 5'-dichloro-2 : 2' : 8-triethylthiacarbocyanine iodide.
Dye IX.	2 : 2' : 8-triethylselenacarbocyanine iodide.
Dye X.	1 : 1'-dimethyl-2 : 2'-carbocyanine iodide.

Parallel with the adsorption measurements, photographic tests were made on plates coated with the dyed emulsion. Spectrograms showing spectral sensitivity were obtained by exposing the plate in a wedge spectrograph, in which an image of a spectrum is projected on the plate, and a measure of relative spectral sensitivity is obtained by having a neutral wedge over the slit. These spectrograms may be used as an estimate of spectral absorption as well as of spectral sensitivity, since it has been shown,<sup>1</sup> for some of the dyes used here, that the two properties are parallel.

The adsorption curves obtained are shown in Figs. 1 and 2, and some corresponding spectrograms in Figs. 3 and 4. (The divisions in the latter figures represent an increase of ten times in the incident intensity and hence in the sensitivity.)

### Discussion.

According to Sheppard, on sensitising a silver halide emulsion with a dye, equilibrium is not reached before 18 hours, using an emulsion diluted by 1 : 25. For the accurate study of adsorption such treatment is necessary, but it is felt that though the results shown here will not correspond to true equilibrium, they will have a closer relation to the practical sensitising results.

The adsorption and sensitising curves of dye V are shown in Figs. 1 and 4. The adsorption curve of this dye is smooth and follows Langmuir's adsorption isotherm, though this latter point is probably fortuitous. The spectrogram shows two regions of sensitivity and therefore light adsorption in addition to the original sensitivity region of the silver halide, with maxima at 520 and 570  $m\mu$ , called here, after Sheppard *et al.*,<sup>4</sup> the  $\alpha$  and  $\beta$  bands respectively. With increasing concentration the relative sensitivity of the two bands increases at about the same rate. Dye IV (Figs. 1 and 3) behaves in the same way, having the  $\alpha$  and  $\beta$  bands at 520 and 580  $m\mu$ . The very similar dye II, however, has an inflection in the adsorption curve (Fig. 1), dye IX (Fig. 2) a more pronounced step, and dye VIII (Fig. 1) a still more definite two-stage adsorption. Examination of the spectrograms (Figs. 3 and 4) show that dye II exhibits principally the  $\alpha$  band at quite low concentration, the  $\beta$  band appearing at higher concentrations. With dyes IX and VIII the  $\beta$  band appears later in the concentration series, parallel with the increased clearness of the two steps in the adsorption curve. It is concluded from these results that the dye is adsorbed in two forms in all cases, but that, as with dyes II, VIII and IX, the  $\alpha$  form is first adsorbed, and then the  $\beta$  form, with, however, more or less overlapping.

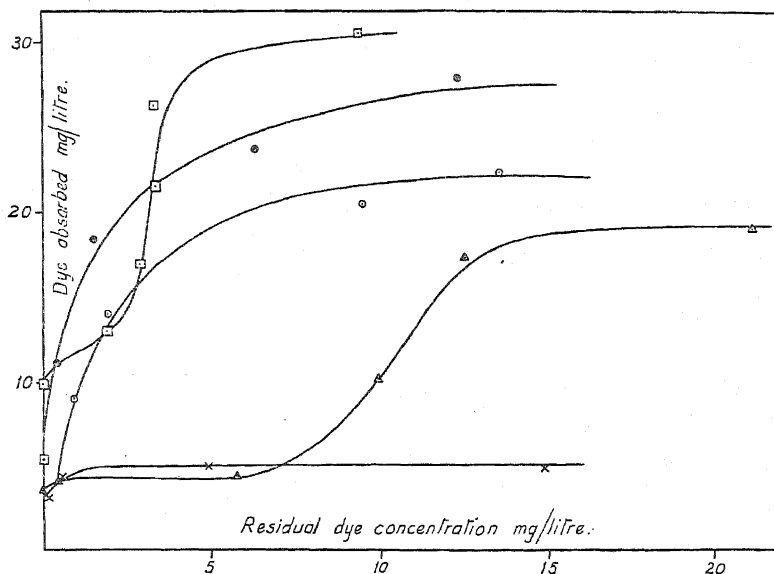


FIG. 1.—Absorption of dyes II, IV, V and VIII.

○ Dye V.      × Dye V (β Band depressed).  
 □ „ II.      ● „ IV.      △ Dye VIII.

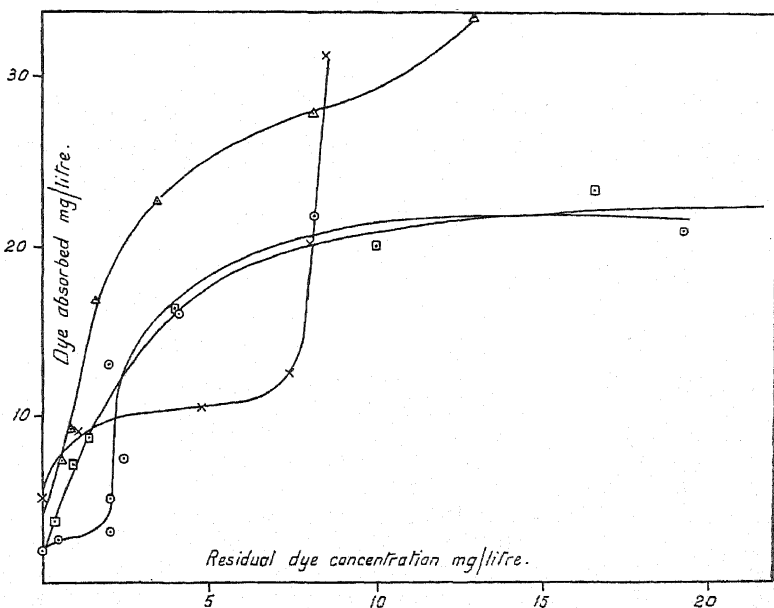


FIG. 2.—Absorption of dyes VII, IX and X.

○ Dye IX.      □ Dye VII.  
 × „ „ (β band depressed).      △ „ X

The saturation level is in all cases of about the same order. Each step may correspond to a unimolecular layer, as suggested by Sheppard *et al.*,<sup>4</sup> who are of the opinion that a first layer is adsorbed, by means of the polar nitrogen atoms of the dye molecule, the rest of the molecule projecting upwards from the surface; a second layer may adsorb to the first, in the reverse way, the polar groups projecting towards the solution. They quote a step-wise curve for dye VII. The curve obtained by the writer for this dye is quite normal (Fig. 2). High dye concentrations led to precipitation of the dye. In this case they used pure silver bromide in the absence of gelatin, but they have also obtained such results in the presence of gelatin. Their first level is approximately half the adsorption level for total adsorption, whereas the first levels

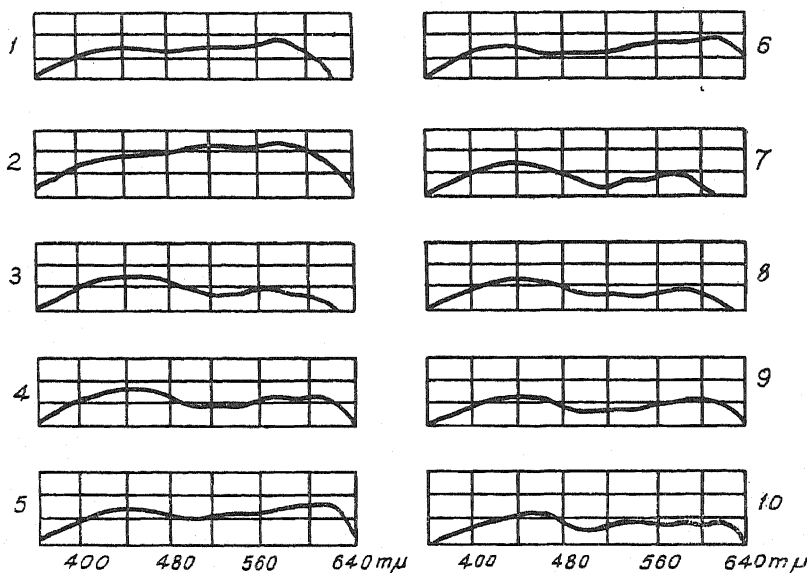


FIG. 3.—Relative spectral sensitivity of dyes II, IV and VII.

1. Dye IV. 4 mg./l. emulsion.	6. Dye II. 20 mg./l. emulsion.
2. " " 20 " "	7. " VIII. 2 " "
3. " II. 1 " "	8. " " 4 " "
4. " " 2 " "	9. " " 10 " "
5. " " 10 " "	10. " " 20 " "

shown here are at varying proportions of total adsorption. It is concluded that the second stage of their adsorption curve for dye VII does probably correspond to a bimolecular layer, but that this may happen only on prolonged tumbling of the diluted emulsion and that the inflections obtained here are in the nature of transition states, which do, however, correspond to the photographic results.

There are substances which depress the  $\beta$  band, more or less, of some dyes, *e.g.*, *o*-phenanthroline in high concentration. Dye V (Figs. 1 and 4), treated in this way, shows only a single level much lower than the usual, and has very little  $\beta$  sensitivity. Dye IX (Figs. 2 and 4) also has a first level only in such circumstances, though higher, corresponding to the higher sensitivity of the  $\alpha$  band, and there is no true saturation level; instead, crystallisation of the dye took place, resulting

in a spurious adsorption curve, for many of the micro-crystals were centrifuged with the silver halide. Dye IX is much less soluble than dye V. Such crystallisation is an explanation of the poor sensitising behaviour of dye X, the dimethyl analogue of the dye VII, as shown in Figs. 2 and 4. The adsorption and sensitising appear weakly at low concentrations, but quite soon crystallisation occurs, as was shown by microscopic examination.

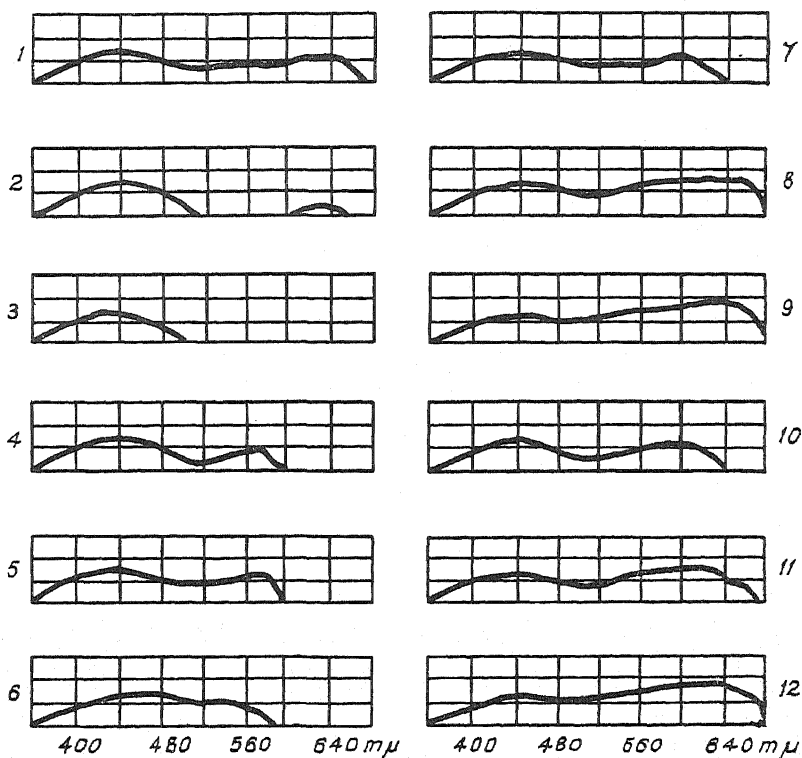


FIG. 4.—Relative spectral sensitivity of dyes V, VII, IX and X.

- |                                 |                               |                           |
|---------------------------------|-------------------------------|---------------------------|
| 1. Dye VII. 10 mg./l. emulsion. | 7. Dye IX. 4 mg./l. emulsion. |                           |
| 2. " X. " " "                   | 8. " " 10 " "                 |                           |
| 3. Unsensitised emulsion.       | 9. " " 20 " "                 |                           |
| 4. Dye V. 4 mg./l. emulsion.    | 10. " " 9 " "                 | } $\beta$ band depressed. |
| 5. " " 20 " "                   | 11. " " 10 " "                |                           |
| 6. " " " " " "                  | 12. " " 20 " "                |                           |
- ( $\beta$  band depressed).

The relation between the light absorption of the dye in different states in solution, and the absorption of the dyed silver halide, has been pointed out by Leermakers *et al.*, and by Sheppard *et al.* They suggest that since the absorption of certain aqueous solutions, in which the dye is most probably aggregated, resembles that of the  $\beta$  form, the latter also represents an aggregated state. Scheibe,<sup>9</sup> in a study of the absorption spectra of various dye solutions, concludes that the separate maxima are due to different states of aggregation. Adsorption from alcoholic solution or from very dilute aqueous solution leads to the  $\alpha$  form only, and hence the latter is assumed to be a unimolecular

form. It need not necessarily be assumed that the state in solution determines the state of the adsorbed dye; the writer has found that successive very small additions of dye II give first the  $\alpha$  form and then the  $\alpha + \beta$  forms, in precisely the same way as when the whole of the dye is added at once. The dye can therefore be adsorbed in single units, whatever the final state on the surface.

The optimum photographic dye concentration is always short of the saturation adsorption level. Leermakers *et al.*<sup>3</sup> and Heisenberg<sup>7</sup> have published data showing the variation of the original blue and of the colour sensitivity with dye concentration, and such figures will therefore not be given here. The amount of dye adsorbed at the photographic optimum is about 60 % of the saturation adsorption level, in the cases of the dyes used here. Leermakers *et al.* found that the amount of dye used/surface of halide ratio was constant for emulsions of different types and varying average grain-size, for any one dye, and concluded that the best explanation of this proportionality between concentration and surface was that a uniform monomolecular layer was formed at the photographic optimum. They calculated that the dye molecules lie flat on the halide surface. However, if in each case the photographic optimum was a constant ratio of the saturation level, this relation would still hold good. Eggert and Biltz<sup>8</sup> also estimated that the dye is approximately unimolecularly adsorbed at optimum sensitisation.

### Conclusions.

To summarise, it has been suggested that the  $\alpha$ - and  $\beta$ -dye forms correspond to single and aggregated molecules respectively, but at the same time, at the photographic optimum, a unimolecular layer has been postulated, with the molecules arranged either flat, or edge-wise, on the silver halide surface. However, at such concentrations, as has been shown here, both forms exist. It is here suggested that the dye molecules are first adsorbed as single molecules, possibly lying flat on the surface, but with subsequent rearrangement at higher concentrations to give an edge-on, closely-packed arrangement, as happens with long-chain fatty acids in water. Scheibe<sup>9</sup> and Jelley<sup>6</sup> have shown that the dye V in certain salt solutions shows the characteristic  $\beta$ -absorption, and, according to Jelley, this may pass into a "nematic" form consisting of thread-like particles oriented in one direction only (as in a pack of cards), and still possessing the  $\beta$ -absorption. Hence the  $\alpha$  form, adsorbed singly, has a light absorption characteristic of the molecule, while the  $\beta$  form, adsorbed edge-on, and packed in a parallel fashion, has an adsorption characteristic of the aggregated or Jelley's nematic form. Cases of suppression of the  $\beta$  form may be explained by assuming that the interfering substance prevents close parallel packing.

### Summary.

Adsorption and sensitising data have been obtained for certain sensitising dyes adsorbed to silver halide. These particular dyes are adsorbed in two forms, each having a distinct absorption, and the two forms are often shown up by two stages in the adsorption curve. From the avail-

<sup>6</sup> E. E. Jelley, *Nature*, 1937, **139**, 631.

<sup>7</sup> E. Heisenberg, *Veroff. Agfa*, 1933, **3**, 115.

<sup>8</sup> J. Eggert and M. Biltz, *Trans. Faraday Soc.*, 1938, **34**, 892.

<sup>9</sup> Scheibe, *Koll. Z.*, 1938, **82**, 1.

able data it is suggested that these dyes are adsorbed partly as single molecules attached by the nitrogen atoms to the surface, but possibly lying flat, and partly as molecules oriented as units packed in a parallel fashion, adsorbed edge-on, again by the nitrogen atoms. The influence of factors which may affect this orientation is discussed.

The author wishes to thank Dr. E. E. Jelley and Dr. S. E. Sheppard for helpful criticisms.

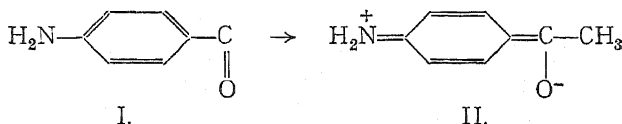
*Research Laboratories,  
Kodak Limited,  
Harrow.*

## ZWITTERION-STRUCTURES IN UNSATURATED CARBONYL COMPOUNDS.

By Miss A. WEIZMANN.

*Received 1st August, 1939.*

In a previous paper,<sup>1</sup> attention has been drawn to the fact that the unexpectedly high dipole-moment (4.29D) of *p*-amino-acetophenone may be accounted for by the assumption that an electron shift has taken place towards a Zwitterion-structure (I  $\rightarrow$  II):



which naturally would exhibit an unusually high electric moment. It is to be expected that analogous, perhaps even more pronounced effects would appear in  $\alpha$ ,  $\beta$ -unsaturated aldehydes and ketones in which the conjugated system is terminated by an amino group.<sup>2</sup> This expectation has been verified by the investigation of the following compounds:—

<i>p</i> -dimethylamido-benzaldehyde	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$	5.6D
<i>p</i> -dimethylamido-cinnamic aldehyde	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CHO}$	5.4D
<i>p</i> -dimethylamido-benzylidene-acetone	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CO} \cdot \text{CH}_3$	5.3D
<i>p</i> -dimethylamido-cinnamylidene-acetone m.p. 120°	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CO} \cdot \text{CH}_3$	6.7D
<i>p</i> -dimethylamido-benzalacetophenone	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$	4.3D
<i>p</i> -dimethylamido-cinnamylidene-acetophenone	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$	5.4D

The effect appears to be more marked with increasing number of double bonds in the conjugated system of the ketones. The same seems to be true for the pair

ethyl <i>p</i> -amino-benzoate	$\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{COOC}_2\text{H}_5$	4.0 <sup>3</sup>
ethyl <i>p</i> -dimethylamino-cinnamate	$\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{COOC}_2\text{H}_5$	4.6;

<sup>1</sup> Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, 32, 1318.

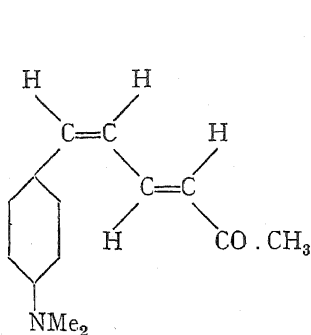
<sup>2</sup> Compare Burawoy, *Ber.*, 1932, 65, 941, 947.

<sup>3</sup> Estermann (*Z. physik. Chem. B.*, 1938, 1, 134) reported the dipole moment 3.3D for methyl *p*-amino-benzoate.

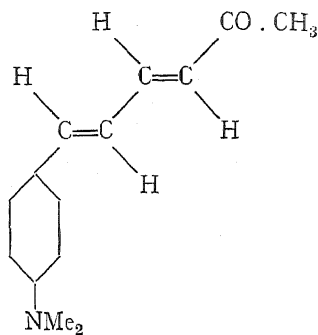


in this case, too, the figures are higher than simple addition of the moments of the amino and the carboxy groups would let us expect. In this respect, the  $\text{C}=\text{O}$  group of the carboxyl behaves like an aldehydic or ketonic carbonyl.

Of *p*-dimethylamido-cinnamylidene-acetone, we have been able to isolate besides the substance listed in the above table a second of the four possible geometric isomers; m.p.  $215^\circ$ . Its dipole moment is distinctly lower ( $2.4\text{D}$ ). This is understood if the polar groups occupy a *c* *is*-position with regard to each other, *e.g.* III instead of IV.



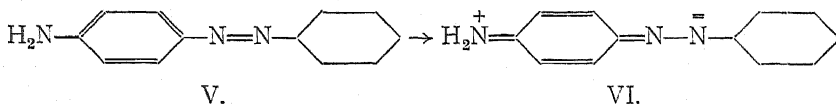
III.



IV.

In connection with these experiments, we have determined the electric moment of *m*-amino-acetophenone; its magnitude ( $5.4\text{D}$ ) seems to indicate that a similar effect occurs as with the isomeric *para*-compound, although no *meta*-quinoidic formulation of this substance is possible.

The intense colour developed by the nitrogen-terminated conjugated systems in, *e.g.*, sulphuric acid, may well be ascribed to a stabilisation of the quinoidic arrangement by addition of the elements of the acid to the charged system.<sup>4</sup> In this connection attention may be drawn to the salt-formation of amino-azo-dyes; for these substances, we have advanced previously the suggestion that they, too, undergo an electron shift in accordance with the scheme  $\text{V} \rightarrow \text{VI}$ .



V.

VI.

On addition of  $\text{HX}$ , V would give the yellow salt, whereas VI, by reaction on the terminal atoms of the charged system, gives the violet isomer, discovered by Hantzsch.<sup>5</sup>

### Experimental.

The figures in the tables have the following significance: *c* molar fraction,  $\rho$  density,  $\epsilon$  dielectric constant, *n* refractive index,  $P_{\frac{1}{2}}$  total polarisation ( $P_{\frac{1}{2}}$  electronic polarisation) for the solution,  $P(P_{\frac{1}{2}})$  the same for the solute,  $P_{A+0}$  atomic and orientation polarisation, which is either graphically extrapolated to infinite dilution or of which the average is taken.

<sup>4</sup> Compare, for a similar case, Wizinger, *Z. angew. Chem.*, 1927, 40, 939.

<sup>5</sup> Hantzsch, *Ber.*, 1909, 42, 2129. It may, however, be noted that according to Kehrman (*Ber.*, 1915, 48, 1933; *Ber.*, 1917, 50, 856) the violet salts need not necessarily be formulated as quinoidic substances.

c.	$\rho$ .	$\epsilon$ .	$n_D^{20}$ .	$P_A^\dagger$ .	$P_{E^\dagger}$ .	P.	$P_E$ .	$P_{A+O}$ .
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***p*-Dimethylamido-benzaldehyde<sup>6</sup> (*t* = 17.5° Benzene).**

o	0.8816	2.2830	2.2251	26.589	—	—	—	—
0.00345	0.8831	2.4815	2.2255	29.291	—	809	calcd.	763
0.00679	0.8846	2.5813	2.2258	30.624	—	621	46	575
0.00878	0.8855	2.7300	2.2261	32.479	—	698	—	652

$$P_{A+O} \text{ (average)} = 664. \quad \mu = 5.6D.$$

***p*-Dimethylamido-cinnamic aldehyde<sup>7</sup> (*t* = 21.3° Benzene).**

o	0.8771	2.2813	2.2457	26.611	26.092	—	—	—
0.00178	0.8788	2.3447	2.2494	27.530	26.153	543	60	483
0.00279	0.8798	2.3990	2.2503	28.295	26.172	630	55	575

(*t* = 27.4°).

o	0.8699	2.2691	2.2323	26.656	26.108	—	—	—
0.00316	0.8713	2.4123	2.2380	28.767	26.254	694	72	622

$$P_{A+O} \text{ (average)} = 598. \quad \mu = 5.4D.$$

***p*-Dimethylamido-benzylidene-acetone<sup>8</sup> (*t* = 24.2° Benzene).**

o	0.8737	2.2754	2.2380	26.632	26.079	—	—	—
0.00280	0.8741	2.3861	—	28.313	—	627	(86)	541
0.00503	0.8744	2.5197	2.2471	30.210	26.382	738	87	651
0.00706	0.8747	2.5878	2.2500	31.169	26.492	669	85	584

$$P_{A+O} \text{ (average)} = 592. \quad \mu = 5.3D.$$

***p*-Dimethylamido-cinnamylidene-acetone<sup>9</sup>; m.p. 120/2° (*t* = 25.4° Benzene).**

o	1.0273	2.2385	2.0116	25.031	21.601	—	—	—
0.00136	1.0269	2.3294	2.0140	26.365	21.692	1006	89	917
0.00196	1.0268	2.3767	2.0150	27.034	21.727	1045	85	960

$$P_{A+O} \text{ (average)} = 939. \quad \mu = 6.7D.$$

<sup>6</sup> Commercial sample; recrystallised from light-petroleum (b.p. 80-100°); m.p. 63°.

<sup>7</sup> Koenig and Schramek, *Ber.*, 1928, 61, 2078. From alcohol, leaflets, m.p. 141°.

<sup>8</sup> In order to obtain *p*-dimethylamido-benzal-acetone, it is necessary to change the conditions stated by Sachs and Lewin (*Ber.*, 1902, 35, 3576): 3 g. dimethylamido-benzaldehyde and 10 c.c. acetone were condensed in 6 c.c. alcohol in presence of some drops of sodium hydroxide solution. From alcohol, m.p. 135-136°. If the aldehyde is condensed with 1.5 g. acetone only, the condensation product, recrystallised from benzene-light petroleum, melts at 191-192° and is bis-*p*-dimethylamido-benzal-acetone (Sachs and Lewin, *l.c.*).

<sup>9</sup> When to a mixture of dimethylamido-cinnamic aldehyde (1.3 g.), acetone (0.3 g.) and alcohol (12 c.c.), a few drops of NaOH solution were added, crystals separated on standing which after treatment with butyl alcohol and recrystallisation from acetone, melted at 215°. The analytical figures concord with the formula of dimethylamido-cinnamylidene-acetone (Found: C, 78.1; H, 6.5.  $C_{14}H_{17}ON$  requires: C, 78.1; H, 7.9 %).

In an experiment, in which 2.5 g. of the aldehyde and 10 c.c. of acetone in 12 c.c. of alcohol were condensed, the reaction product, after recrystallisation from benzene, had m.p. 120-122° and gave the same analytical figures (Found: C, 77.4; H, 7.6.  $C_{14}H_{17}ON$  requires: C, 78.1; H, 7.9 %).

c.	$\rho$ .	$\epsilon$ .	$n_D^{25}$ .	$P_H^1$ .	$P_{E_H}^1$ .	P.	$P_E$ .	$P_{A+O}$ .
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**p-Dimethylamido-benzal-acetophenone**<sup>10</sup> ( $t = 20.3^\circ$  Benzene).

0	0.8783	2.2834	2.2440	26.609	26.061	—	—	—
0.00276	0.8791	2.3536	2.2515	27.799	26.279	457	105	352
0.00316	0.8794	2.3927	2.2533	28.358	26.355	491	104	387
0.00642	0.8801	2.5056	2.2596	30.034	26.578	560	106	454

 $P_{A+O}$  (average) = 398.  $\mu = 4.4D$ .**p-Dimethylamido-cinnamylidene-acetophenone**<sup>11</sup> ( $t = 26.0^\circ$  Dioxan).

0	1.0272	2.2301	2.0135	24.911	21.634	—	—	—
0.00147	1.0279	2.2917	2.0203	25.848	21.796	660	132	528
0.00216	1.0282	2.3431	2.0224	26.590	21.855	803	124	679
0.00324	1.0286	2.3806	2.0278	27.151	21.983	716	129	587

 $P_{A+O}$  (average) = 598.  $\mu = 5.4D$ .**Ethyl p-amino-benzoate**<sup>12</sup> ( $t = 19.4^\circ$  Benzene).

0	0.8794	2.2852	2.2500	26.603	26.088	—	—	—
0.00386	0.8813	2.3962	2.2524	28.229	26.174	447	48	399
0.00620	0.8825	2.4311	2.2512	28.743	26.193	372	49	323
0.00848	0.8837	2.4659	2.2536	29.247	26.260	339	46	293

 $P_{A+O}$  (average) = 340.  $\mu = 4.0D$ .**Ethyl p-dimethylamino-cinnamate**<sup>13</sup> ( $t = 18.8^\circ$  Benzene).

0	0.8801	2.2964	2.2407	26.599	25.929	—	—	—
0.00480	0.8828	2.4541	2.2545	29.097	26.280	547	99	448
0.00676	0.8838	2.5312	2.2563	30.188	26.368	556	91	465

 $P_{A+O}$  (average) = 457.  $\mu = 4.6D$ .**p-Dimethylamido-cinnamylidene-acetone** (m.p.  $215^\circ$ )<sup>9</sup> ( $t = 20.0^\circ$  Dioxan).

0	1.0284	2.3141	2.0170	26.065	21.664	—	—	—
0.00040	1.0314	2.3239	2.0218	26.138	21.690	210	87	123

 $\mu = 2.4D$ **m-Amino-acetophenone**<sup>14</sup> ( $t = 18.2^\circ$  Benzene).

0	0.8808	2.2876	2.2515	26.995	26.069	—	—	—
0.00457	0.8827	2.4541	2.2530	28.945	26.122	541	38	503
0.00747	0.8839	2.4999	2.2536	29.574	26.151	426	37	389
0.01078	0.8852	2.5435	2.2560	30.165	26.208	363	39	324

 $P_{A+O}$  (average) = 635.  $\mu = 5.4D$ .<sup>10</sup> Sachs and Lewin, *l.c.*<sup>8</sup> From alcohol, m.p.  $114^\circ$ .<sup>11</sup> Dimethylamido-cinnamic aldehyde (1 g.) and acetophenone (1.5 g.) were gently heated in alcohol (10 c.c.) in presence of a few drops of NaOH solution for 5 minutes. On cooling, brown, shiny needles separated, which after recrystallisation from methyl alcohol, had m.p.  $155-157^\circ$ ; yield 0.6 g. (Found: C, 83.0; H, 6.3.  $C_{18}H_{15}ON$  requires: C, 82.3; H, 7.0 %).<sup>12</sup> Commercial sample; from alcohol, m.p.  $91-92^\circ$ .<sup>13</sup> Sodium wire (2.3 g.) is suspended in ethyl acetate (20 g.) and a solution of p-dimethylamido-benzaldehyde (14.9 g.) in ethyl acetate (30 g.) is added. The reaction is slow, but goes to complete solution of the sodium. Glacial acetic acid (5 g.) is added, the product washed with water, dried with sodium sulphate and evaporated. The residue is recrystallised from light-petroleum (b.p.  $80-100^\circ$ ); m.p.  $70^\circ$ . Weil, *Monatshefte*, 1908, **29**, 900.<sup>14</sup> Acetophenone was nitrated according to Elson, Gibson and Johnson (*J. Chem. Soc.*, 1930, 1130) and the m-nitro-compound reduced in the following way: 10.5 g. were mixed with 24 g. granulated tin and gently heated. Then concentrated hydrochloric acid was added in small quantities, until all the metal had dissolved. Alkali was added and the amino-compound isolated by extraction with ether (yield, 5 g.). Recrystallisation from benzene gave slightly yellowish plates, m.p.  $99^\circ$ .

### Summary.

The occurrence of Zwitterion-structure is detected in compounds of the *p*-dimethyl-amido-benzaldehyde, *p*-dimethylamido-benzal-acetophenone and ethyl *p*-amino-benzoate type by means of dipole-moment measurements. The difference in electric moment of two isomeric dimethyl-amido-cinnamylidene-acetones obtained is discussed.

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## AN INFRA-RED STUDY OF CHLORAL HYDRATE AND RELATED COMPOUNDS.

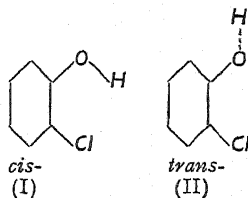
BY MANSEL M. DAVIES.

*Received 14th August, 1939.*

The inter- and intra-molecular interactions of polar groups have recently been the subject of many spectroscopic investigations.<sup>1</sup> In particular, the influence of both molecular association and of adjacent substituents upon the valence vibration of the OH group has been observed in infra-red absorption spectra. The present paper is principally concerned with the second mode of interaction. It may be taken in three sections: the first presents some new experimental observations on absorption spectra of this type; the second is concerned with the evaluation of bond-energy differences from frequency changes; whilst the third discusses the probable origin of these energy differences.

### PART I.

The clearest example of the effects studied is that of *o*-chlorophenol<sup>2</sup> where the interaction of the Cl and OH groups leads to two orientations of the latter, the *cis*- form (I) being favoured with respect to the *trans*- (II) by an amount corresponding to an energy difference of about 1400 cal./g. mol. It is now to be established that a similar interaction is responsible for the peculiar stability of chloral hydrate,  $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$ . This compound and its analogue bromal hydrate are the only two common stable derivatives in which two hydroxyl groups are attached to the same carbon atom.



### Experimental.

The methods were essentially those previously described.<sup>3</sup> A Nernst glower was throughout the source of radiation. Quartz, fluorite, and rock-salt prisms have been employed in the present measurements and a rock-

<sup>1</sup> Sutherland, *Ann. Rep. Chem. Soc.*, 1938, **35**, 38.

<sup>2</sup> Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94. Davies, *Trans. Faraday Soc.*, 1938, **34**, 1427.

<sup>3</sup> Davies and Sutherland, *J. Chem. Physics*, 1938, **6**, 755.

salt cell of similar construction to the fluorite ones has been used beyond  $10\ \mu$ . Analar solvents were used without further purification. The solvent corrections were repeatedly checked between the runs made with the solutions, and all the absorption curves reproduced have been corrected for the cell and solvent effects. The chloral and bromal hydrates were purchased from Messrs. Harringtons: careful recrystallisation from  $\text{CS}_2$  had no noticeable effect on their absorption spectra. The setting of the prisms was done with the visible lines from a small Hg-discharge tube, and subsequently checked on the sharp OH absorption band in dilute  $\text{CCl}_4$  solutions of benzyl alcohol at  $2.764\ \mu$ : for the fluorite and rock-salt prisms the  $4.26\ \mu$  atmospheric  $\text{CO}_2$  band was plotted for confirmation.

### Results.

A determination of the absorption of chloral hydrate in the region  $2.6\ \mu$  to  $3.0\ \mu$  in  $\text{CCl}_4$  shows the significant result that the OH band in

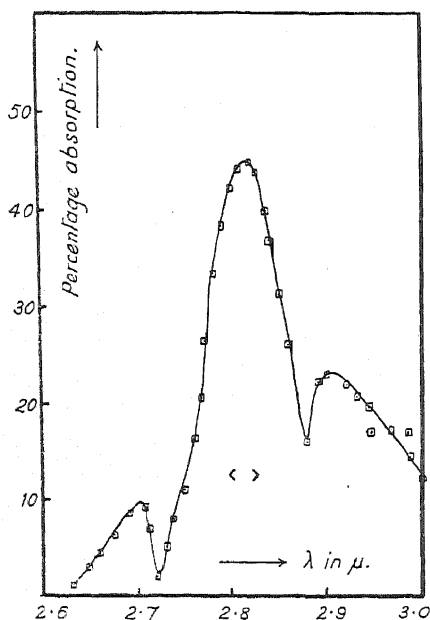


FIG. 1.—Absorption of 5.0 mm. layer of 0.006 M. chloral hydrate in  $\text{CCl}_4$ .

this molecule is centred at  $2.82\ \mu$ . Fig. 1 shows a typical curve for a saturated solution in  $\text{CCl}_4$ . The main band is located at  $2.82\ \mu$ , whilst weaker peaks appear at  $2.70\ \mu$  and  $2.90\ \mu$ . Of these feebler absorptions, that at  $2.70\ \mu$  is certainly an overtone or combination band characteristic of the  $\text{CCl}_3$  group, as it occurs in all the compounds containing this structure which have been examined;<sup>3</sup> the shoulder at  $2.90\ \mu$  is probably a combination band involving the C—O frequencies.

The position and intensity of the  $2.82\ \mu$  band leave no doubt as to its origin. The concentration of the chloral hydrate in the solution used was estimated as about 0.0060 M., and the considerable intensity of the band under these conditions is typical of the OH group. The

only other common fundamentals occurring in this region are those of the C—H bond which appears in the range  $3.25\ \mu$  (aromatic) to  $3.45\ \mu$  (aliphatic), and of the NH group which is near  $3.00\ \mu$ . Attempts to confirm the origin of the  $2.82\ \mu$  absorption by observations on  $\text{CCl}_4$  solutions of chloral ( $\text{CCl}_3 \cdot \text{CHO}$ ) in the same region failed because these solutions rapidly became saturated with the hydrate due to absorption of atmospheric moisture during the filling of the cell. Only by twice distilling the hydrate from concentrated  $\text{H}_2\text{SO}_4$  in an all-glass apparatus protected by a stream of dry air could the chloral be satisfactorily freed from the hydrate and exposure to moist air quickly led to the formation of sufficient hydrate for this to crystallise out. Chloroform,  $\text{HCCl}_3$ , and ethyl ether,  $\text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5$ , which together contain

all the groups and bonds present in chloral hydrate other than the hydroxyl, show at concentrations 100 times greater than those of the hydrate no signs of an absorption centred near  $2.82 \mu$ .

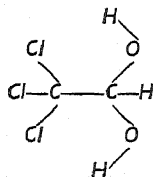
It is now well established<sup>4</sup> that simple alcohols in dilute  $\text{CCl}_4$  solution have a sharp absorption band arising from the valence OH vibration the peak of which is within the range  $2.750 \mu$  to  $2.770 \mu$ . On the attachment of a carbonyl oxygen to the same carbon atom as the

hydroxyl, *i.e.*, in  $\text{—C} \begin{array}{l} \text{=O} \\ \text{—OH} \end{array}$  the interaction of the  $\text{C=O}$  and  $\text{O—H}$

groups shifts the fundamental band of the latter to  $2.84 \mu$ . Compared

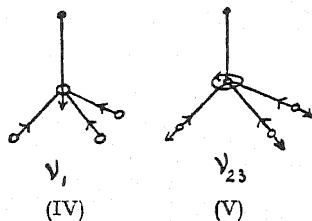
with a simple hydroxylic compound such as methyl alcohol,  $\text{CH}_3\text{—O—H}$ , where the potential barrier restricting free rotation of the hydrogen about the  $\text{C—O}$  bond is small,<sup>5</sup> in the carboxyl structure the OH group is now locked in the *cis*-position.<sup>6</sup> The same shift to longer wavelengths of the OH fundamental is also apparent as between *trans*- and *cis*-*o*-chlorophenol (from  $2.775 \mu$  to  $2.825 \mu$ ). It seems certain that the location of the OH fundamental in chloral hydrate at  $2.82 \mu$  arises from circumstances similar to those just mentioned. It suggests that the OH groups are again clamped in a position corresponding to maximum interaction with the adjacent dipoles, each OH group lying

in the plane defined by a  $\text{Cl—C—C}$  group, with the hydrogens tied towards the chlorines (III). It can easily be seen that if the hydrogens were free to rotate about the  $\text{C—O}$  bonds they might approach one another very closely and the elimination of  $\text{H}_2\text{O}$  would then be a simple process. Several careful plots of the band have failed to show any indication of even a shoulder in the absorption curve near  $2.76 \mu$  so that the occurrence of structures, in which one of the OH groups is free, is not detectable. The band does appear to be broader than that for a monohydroxylic alcohol examined under the same conditions. It may be that, the restoring force governing the vibrations of the



(III)

hydrogens perpendicular to the  $\text{Cl—C—C—O}$ -plane being small, the amplitude of this vibration is responsible for a slight variability in the force-constant of the valence  $\text{O—H}$  vibration.



(IV)

(V)

Having established the distinctive change in the OH frequency, it was of interest to investigate whether the interaction was also noticeable by its influence on the  $\text{CCl}_3$  group. A major uncertainty in the interpretation of these results lies in the assignment of the  $\text{CCl}_3$  frequencies which, in the absence of a complete vibrational analysis, has to be made largely by comparison

<sup>4</sup> Fox and Martin, *Proc. Roy. Soc., A*, 1937, **162**, 419.

<sup>5</sup> Borden and Barker, *J. Chem. Physics*, 1938, **6**, 553.

<sup>6</sup> Bauer and Badger, *ibid.*, 1937, **5**, 852. Morino and Mizushima, *Proc. Instit. Phys. Chem. Research, Tokyo*, 1937, **32**, 33. Davies and Sutherland,<sup>8</sup> p. 762. See, however, Coop, Davidson and Sutton, *J. Chem. Physics*, 1938, **6**, 905.

with the simpler molecule,  $\text{CHCl}_3$ . According to Kohlrausch<sup>7</sup> the two valence vibrations for  $\text{CHCl}_3$  (IV and V) (of which  $\nu_{23}$  is doubly degenerate) are to be assigned as  $\nu_1 = 668 \text{ cm.}^{-1}$ ,  $\nu_{23} = 760 \text{ cm.}^{-1}$ ,<sup>8</sup> which would correspond to absorption bands at  $15.0 \mu$  and  $13.2 \mu$  respectively.

A careful examination of the absorptions of chloral hydrate and trichloroacetic acid in the region  $11 \mu$  to  $15 \mu$  was made using a rock-salt prism: trichloroacetic acid was chosen for comparison as being the molecule nearest in structure to chloral hydrate. Several measurements of trichloroacetic acid in  $\text{CS}_2$  (Fig. 2) show two distinct bands. One, centred at  $14.25 \pm 0.1 \mu$  seems to be the equivalent of  $\nu_1$  in  $\text{CHCl}_3$ : its contour suggests the appearance of the *P*-, *Q*-, and *R*-branches of a parallel vibration. The second has its main peak at  $12.2 \mu$  with a subsidiary at  $12.7 \mu$ : a doublet nature is to be expected for  $\nu_{23}$  in this case, as the degeneracy is now removed. Absorption curves for chloral hydrate in  $\text{CS}_2$  (Fig. 3) similarly showed peaks at  $12.35 \mu$  and  $12.75 \mu$

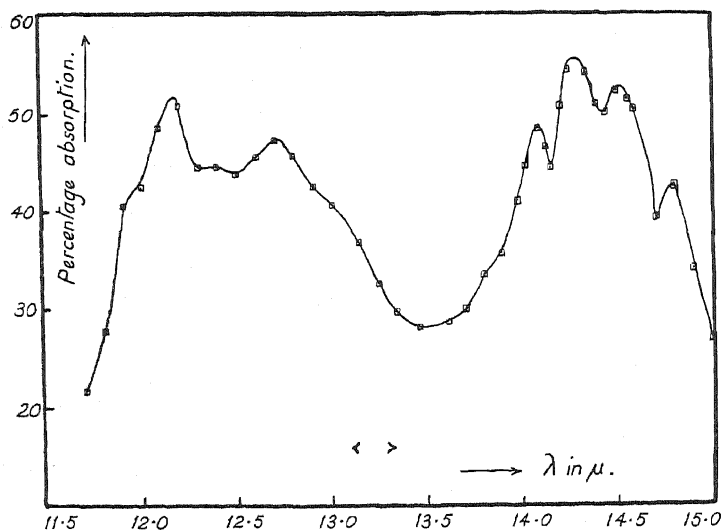


FIG. 2.—Absorption of 1.5 mm. of 0.057 M. trichloroacetic acid in  $\text{CS}_2$ .

almost coinciding with those in the acid. The centre of what has been taken as the  $\nu_1$  band, however, is now located at  $13.7 \mu$  which is far removed from its position in trichloroacetic acid, amounting to a frequency shift of  $28 \text{ cm.}^{-1}$ . The higher frequency of  $\nu_1$  in chloral hydrate compared with the acid is not what would have been expected if the interaction in the former merely led to the C—Cl bond being stretched along its length. The result may mean that the principal effect consists in a lateral displacement of the Cl atoms opposite the hydrogens, which in itself would probably result in a steeper potential curve along the C—Cl direction. It is to be noted that the present interpretation of these results does not conflict with the Raman data for these molecules.<sup>8a</sup>

There is a further fundamental of the  $\text{CCl}_3$  group, which Kohlrausch surprisingly assigns to a deformation vibration, at  $1215 \text{ cm.}^{-1}$ , *i.e.*,

<sup>7</sup> *Z. physik. Chem., B*, 1935, **28**, 340.

<sup>8</sup> Cabannes and Rousset, *Ann. Physique*, 1933, **19**, 229; and ref. 7.

<sup>8a</sup> Parthasarathy, *Phil. Mag.*, 1934, **17**, 471. Kohlrausch, Koppland Pongretz, *Z. physik. Chem., B*, 1933, **21**, 242.

within the experimental infra-red range, at  $8.2\ \mu$ . The region  $7.5\ \mu$  to  $8.5\ \mu$  was examined, using a fluorite prism. The absorption curve

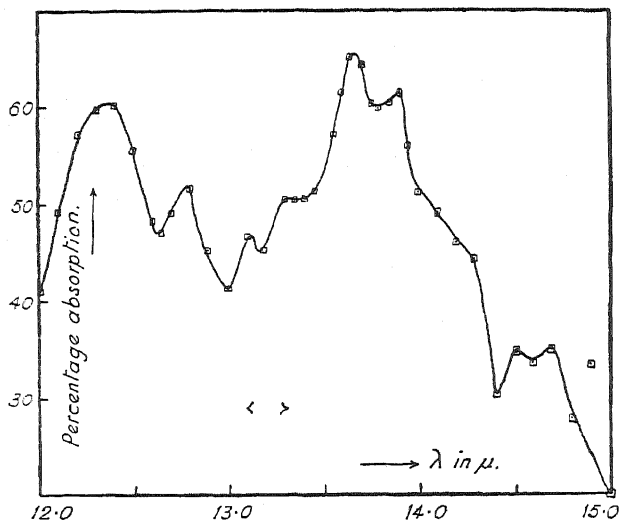


FIG. 3.—Absorption of saturated solution chloralhydrate in  $\text{CS}_2$ . Cell thickness =  $1.5\ \text{mm}$ .

for trichloroacetic acid was found to have a strong band at  $7.96\ \mu$  with shoulders at  $7.87\ \mu$ ,  $8.16\ \mu$ , and  $8.24\ \mu$ , the central peak, from its intensity, almost certainly corresponding to a fundamental. Plots made of chloral hydrate showed the main absorption at  $8.21 \pm 0.01\ \mu$ , but subsidiary bands in the neighbourhood are so numerous as to make interpretation far too speculative.

**Bromal Hydrate.** (Fig. 4). This compound has been examined only in the short-wave region of the OH fundamental. In both  $\text{CS}_2$  and  $\text{CCl}_4$  solutions the main absorption is at  $2.81 \pm 0.01\ \mu$ . In the five plots of this absorption which have been made there are indications, although these are admittedly slight, of an irregularity corresponding to an absorption at  $2.76\ \mu$ . The latter might well arise from a small proportion of "free" OH groups, the presence of which would coincide with the lower stability of bromal hydrate relative to chloral hydrate. The published measurements on water in these two solvents<sup>9</sup> show that in

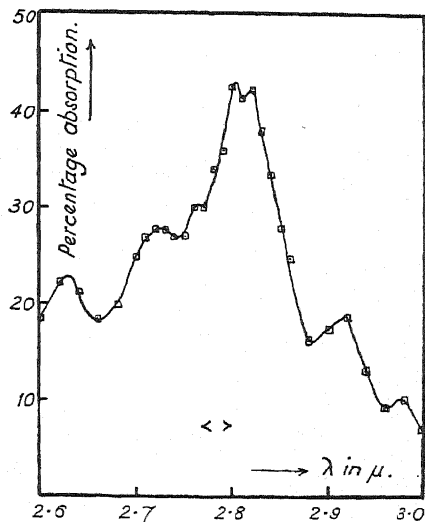


FIG. 4.—Absorption of bromal hydrate in  $\text{CS}_2$ . Nearly saturated solution in  $25\ \text{mm}$ . cell.

<sup>9</sup> Borst, Buswell and Rodebush, *J. Chem. Physics*, 1938, 6, 61. Kinsey and Ellis, *Physic. Rev.*, 1937, 51, 1074.



$\text{CCl}_4$  it gives only a single absorption at  $2.70\ \mu$ , whilst in  $\text{CS}_2$  the absorption of a saturated solution is far too small to have been recorded in the present measurements.

**Benzoin.** (Fig. 5). Several measurements of  $\text{CCl}_4$  solutions of benzoin,

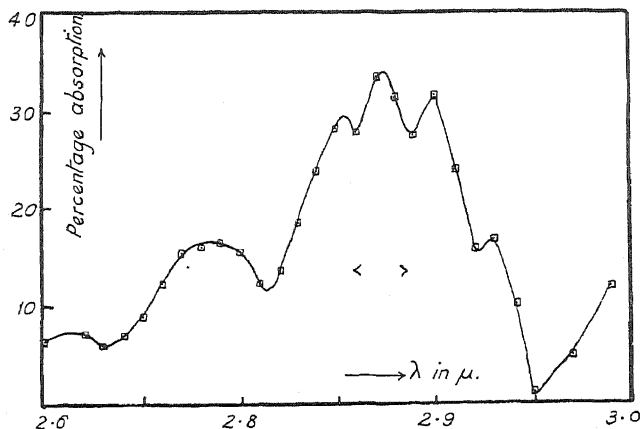


Fig. 5.—Benzoin in  $\text{CCl}_4$  solution saturated at room temperature. 3.05 mm. cell.

$\text{C}_6\text{H}_5 \cdot \text{CHOH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , have been made and two broad but easily separable absorptions were found near  $2.78\ \mu$  and  $2.89\ \mu$ ; these must be attributed to the different orientations of the OH group with respect

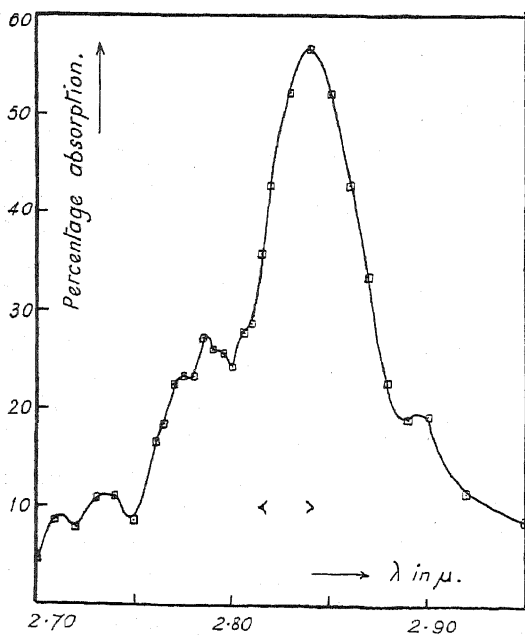


Fig. 6.—0.090 M. o-bromophenol in  $\text{CCl}_4$  at  $17^\circ\text{C}$ . 3.05 mm. cell.

to the  $\text{C}=\text{O}$  group. The abnormal breadth of these OH absorptions is also apparent in the overtone region,<sup>10</sup> and the one at  $2.89\ \mu$  has now been resolved into a number of peaks. So different is this from the usual appearance of these bands that their identification was confirmed by examining benzophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  in the same region, throughout which it was found to have no appreciable absorption. The peculiar width of the bands is presumably due to the coupling of the OH frequencies with other much

lower frequencies in the molecule, but why this should be so pronounced

<sup>10</sup> Wulf and Liddel, *J. Amer. Chem. Soc.*, 1935, 57, 1464.

in the present instance is not clear. Although the estimate of the band intensities was not very reliable owing to their width, it sufficed to show the increase of the  $2.78 \mu$  absorption relative to the  $2.89 \mu$  with rising temperature.

**Ortho-bromophenol.** (Fig. 6). This solute was carefully examined at both room temperature and at  $75^\circ \text{C}$ . in  $\text{CCl}_4$ . The main absorption consists of a symmetrical peak at  $2.84 \mu$ , whilst a small but less regular absorption, centred at  $2.785 \mu$ , was also shown. These correspond to the *cis*- and *trans*- forms respectively. From the integrated absorptions  $\left( \delta = \int \log_{10} \frac{I_0}{I} d\lambda = kcl \right)$ , making allowance for the overlapping of the bands, the relative concentrations were found to be  $4.31:1$  at  $17^\circ$  and  $2.95:1$  at  $75^\circ$ . Assuming an equilibrium determined by a statistical factor  $e^{\delta/RT}$ , the values of the energy difference of the isomers would be  $850$  and  $760 \text{ cal./g. mol.}$ , from which a mean value of  $800 \text{ cal./g. mol.}$  may be accepted.

## PART II.

In this section the relation of the frequency change in the OH group between two structures and the corresponding energy difference will be discussed on the basis of the results now available. The lowering in frequency on association of the alcohols was linked by Fox and Martin<sup>11</sup> with the energy involved on the basis of the Morse potential function. The latter gives for the energy of dissociation from the vibrationless level,  $D = \frac{h\omega_e(1-x)^2}{4x}$ , where  $\omega_e$  is the vibration frequency for ideally small displacements and  $x$  is the anharmonicity factor:  $\omega_e$  is related to the observed frequencies by  $\nu_n = n\omega_e[1 - (n+1)x]$ , where  $n = 1$  for the fundamental,  $n = 2$  for the first overtone, etc. Clearly if  $x$  is the same for the two forms of the molecule,  $\delta D/D = \delta\omega_e/\omega_e$  and their energy difference  $\delta D$  can be estimated directly from  $\delta\omega_e$  using a reasonable value for  $D$ , the dissociation energy of the hydroxyl group (e.g.,  $113 \text{ k. cal./g.mol.}$ ).

A direct test of the identity of  $x$  for the two forms of each molecule is very desirable, but only for *o*-chlorophenol and *o*-bromophenol are the locations of the origins of the relevant absorptions sufficiently precise to give significant results. These are shown in Table I.

The figures in brackets involve a frequency observed in the pure substance: the others refer to  $\text{CCl}_4$  solutions. There seems little doubt that  $x$  varies by about 10 per cent. between the two forms of the same molecule. It has been confirmed that with the data at present available (e.g., for benzoin, monomeric and dimeric acetic acid, monomeric and associated alcohols) the evaluation in this way of the energy difference between two molecular configurations as the simple difference of their  $D$  values gives only such meaningless results as in Table I, where these differences have the wrong sign. This general anomaly partly results from the fact that the anharmonicity factor is found to be larger for the form in which interaction occurs.

Returning to the simplified relation used by Fox and Martin, Table II shows the values of  $\delta D = \frac{\delta\omega_e}{\frac{1}{2}(\omega_1 + \omega_2)} \times 113 \text{ k. cal./g. mol.}$

<sup>11</sup> See ref. 4.

The corresponding values to  $\delta D$  from other methods are given in the last column.

The spectroscopic estimates of the energy differences are obviously only of the correct order of magnitude, although it must be emphasised that, except in the case of the carboxylic dimer, more accurate values are also desirable for the last column.

TABLE I.\*

Compound.	Frequency (cm. <sup>-1</sup> ).	$\pi \cdot 10^2$ .	$\omega_e$ .	$D$ (k. cal./g. mol.).
<i>Cis</i> -chlorophenol . .	3540 } 6910 } 10086 } (12993)	2.29 } 2.34 } 2.60 } 2.34	3714	107.7
<i>Trans</i> -chlorophenol . .	3603 } 7050 } 10331 } (13328)	2.08 } 2.12 } 2.39 } 2.10	3760	122.1
<i>Cis</i> -bromophenol . .	3520 } 10001 }	2.51	3710	99.95
<i>Trans</i> -bromophenol . .	3595 } 10317 }	2.08	3760	123.37

\* (Data taken from Freymann, *J. Physique et Radium*, 1938, 9, 517; Davies, *Trans. Faraday Soc.*, 1938, 34, 1427.)

A linear relation between  $\delta D$  and  $\frac{\delta\omega_e/\omega_e}{\omega_e}$  is also to be expected on the basis of a simple potential function recently suggested by Sutherland<sup>12</sup> as a useful representation of the conditions in diatomic linkages. This is partly borne out by the fact that the spectroscopic values in Table II are about double the estimates otherwise made. This empirical correspondence is probably the best which can be attained at present.

TABLE II.

Molecule.	Structure.	$\nu$ (fundamental).	$\pi \times 10^2$ .	$\omega_e$ .	$\delta D$ .	$\delta E$ .
<i>o</i> -Chlorophenol	<i>cis</i> -	3540	2.22	3704	2.06	1.4 to 1.7
	<i>trans</i> -	3603		3772		
<i>o</i> -Bromophenol	<i>cis</i> -	3520	2.30	3690	2.31	0.8
	<i>trans</i> -	3595		3768		
Benzoin .	<i>cis</i> -	3454	2.20	3613	4.80	—
	<i>trans</i> -	3604		3770		
Acetic acid .	monomer	3525	2.00	3672	17.2	7.8
	dimer	3030		3155		
Ethyl alcohol .	monomer	3634	2.20	3802	8.42	4.0
	associated	3373		3529		

## PART III.

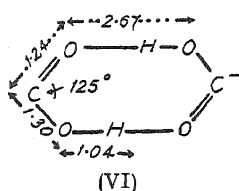
Perhaps the major interest in the molecular systems being discussed lies in the determination of the origin of the interaction energies concerned. It is the object of the present section to indicate that in many

<sup>12</sup> *Proc. Indian Acad. Sci.*, 1938, 8, 341.

cases, at least, these may be accounted for by dipole interactions with the addition of the induction and possibly dispersion effects. The origin and magnitude of these forces have been clearly discussed in a summarising paper by London.<sup>13</sup>

In this respect the carboxylic acid dimer is the most instructive example, as both its structure and the experimental value of  $\delta E$  are accurately known. For the former the data<sup>14</sup> lead to the representation shown (VI), where distances are in Angstrom units. In the subsequent calculations, unless otherwise specified, interatomic distances and dipole moments have been taken from Pauling's book,<sup>15</sup> and most of the group polarisabilities ( $\alpha$ ) from Waters.<sup>16</sup> In the present instance, we have taken  $\mu_{C=O} = 2.50D$ ,  $\mu_{O-H} = 1.66D$ ,  $\mu_{C-O} = 0.7D$  (the last

TABLE III.



<div>In (A)→</div> <div>↓ In (B).</div>	O—H.	C—O.	C=O.
C=O	−5955	+883	−1680
C—O	+455	−144	+883
O—H	−148	+455	−5955

from Sidgwick and Bowen<sup>17</sup>);  $\alpha_{C=O} = 1.35$ ,  $\alpha_{O-H} = 1.0$ ,  $\alpha_{C-O} = 2.0$ , in units of  $10^{-24}$  c.c. In calculating the interactions an accurate scale model of the planar group has been drawn and the distances required obtained from this. For the simple dipole interaction the moments have been resolved into point charges located at the appropriate atomic centres. Taking the separate interactions of each group in one half (A) of the carboxylic dimer with those in the other half (B), a total Coulombic contribution to  $\delta E$  of  $-11,200$  cal./g. mol. is obtained, distributed as in Table III:

The value  $-5955$  cal. for the  $C=O$  and  $OH$  interaction is in agreement with the similar values for this factor previously calculated by a different method by Moelwyn-Hughes.<sup>18</sup>

The induction effect for a dipole  $\mu_1$  orientated at an angle  $\theta_1$  to the line joining its centre to that of a group of polarisability  $\alpha_{11}$  is given by

$$U = -\frac{\alpha_{11}}{2} \cdot \frac{\mu_1^2}{R^6} (1 + 3 \cos^2 \theta_1) : R \text{ is the distance between the centres of the interacting systems. This energy, being necessarily negative, invariably corresponds to an attraction. For the total interaction between two groups the contributions of } \mu_1 \text{ and } \alpha_{11}, \mu_{11} \text{ and } \alpha_1 \text{ must be added. Thus, the total energy in the present instance will be the sum of eighteen terms of the form above, and this total is found to be } 2240 \text{ cal./g. mol.}$$

It remains to evaluate the dispersion interaction for which London, in the same circumstances as the above, has given the expression

$$U = -m_1^2/3hR^6 \cdot (1 + 3 \cos^2 \theta_1) \cdot \sum \frac{m_2^2 \nu_2}{\nu_2^2 - \nu_1^2}. \text{ Here } m_1 \text{ is the "oscil-}$$

<sup>13</sup> *Trans. Faraday Soc.*, 1937, **33**, 8.

<sup>14</sup> Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.

<sup>15</sup> *The Nature of the Chemical Bond*, Cornell Univ. Press, 1939, p. 146.

<sup>16</sup> *J. Chem. Soc.*, 1933, 1551.

<sup>17</sup> *Ann. Rep. Chem. Soc.*, 1931, **28**, 402.

<sup>18</sup> *J. Chem. Soc.*, 1938, 1243.

lator strength" appearing in the simple dispersion formula which gives the polarisability  $\alpha_1$  of the group, of which  $\nu_1$  is the resonance electronic frequency. To evaluate these terms, the approximate relation  $m_1^2 = 3\hbar\nu_1\alpha_1/2$  is combined with the assumption that  $\nu_1$  may be identified with the frequency corresponding to the ionisation potential ( $V_1$ ) of the same group ( $\hbar\nu_1 = eV_1$ ): at the same time this involves the replacement of the summation by a single term. It is obvious from the appearance of the term  $(\nu_2^2 - \nu_1^2)$  that the net interaction of two groups will be the difference of two terms: e.g., the C=O group acting on the OH of the opposite molecule leads to  $U = -7380$  cal.: the OH acting on the C=O gives  $U = +10,590$  cal. This gives the impossible result of a net repulsion of 3210 cal. between these two groups: impossible, because the dispersion effect must necessarily lead to an attraction. A great proportion of the error in this evaluation is introduced in the substitution used for  $m_1^2$ . This is avoided in the case of two groups at random orientation with respect to one another, for which the total dispersion interaction simplifies to

$$U = -3\hbar/2R^6 \cdot \alpha_1\alpha_{11} \cdot \frac{\nu_1\nu_{11}}{\nu_1 + \nu_{11}}.$$

At their distance apart, the groups mentioned (if at random orientation) would yield an attractive energy of 1090 cal./g. mol. This is certainly a better estimate of the true order of magnitude of the dispersion energy. For the other groups, owing to the  $R^{-6}$  term, this contribution is bound to be much smaller, and for the present it is neglected.

It is noticeable in these circumstances that the dipole interaction is certainly much greater than the dispersion effect. This order is contrary to their contribution to the van der Waals forces in many instances.<sup>19</sup> But the reason is not far to seek. The interatomic distances here dealt with are too small to make the condition  $\frac{\mu_1\mu_2}{R^3} \ll kT$  necessitated in London's comparison of these forces of any further validity. Thus, for the C=O and O—H groups,  $\frac{\mu_1\mu_2}{R^3} = 26.5 \times 10^{-14}$  ergs per molecule, compared with  $kT = 4.0 \times 10^{-14}$  at room temperatures. Further, the fixed orientation of the dipoles with respect to one another, means that their interaction approaches the maximum possible ( $U = -\frac{2\mu_1\mu_2}{R^3}$ ) where the dependence is upon  $R^{-3}$ , rather than  $R^{-6}$  as occurs for the random orientation at large distances involved in the van der Waals forces.

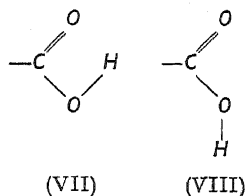
It has been found that the simple and induced dipole effects together give an interaction energy of 13,440 cal./g. mol., compared with a measured  $\delta E$  for formic and acetic acids in the gas phase<sup>20</sup> near 15500 cal./g. mol. In the first place, it may safely be suggested that the difference, 2060 cal. or 13 per cent., may be attributed to the dispersion forces. This proportion might well be used as a fair estimate of the relative contribution of this effect as between orientated groups in molecular structures: for the 13 per cent. in the present instance is the mean over several groups at various distances. Further, the fact

<sup>19</sup> London, *loc. cit.* <sup>13</sup>, p. 19.

<sup>20</sup> MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585. Coolidge, *ibid.*, 1928, **50**, 2166.

that 87 per cent. of the observed interaction energy can be accounted for on the simple basis of electrostatic forces makes the introduction of any resonance effects connected with a "hydrogen bond" of small import in this case. This conclusion agrees with the general sense of the spectroscopic analysis of this structure.<sup>3</sup>

**The Monomeric COOH Group.** A simpler example of the operation of the foregoing effects is found in the structure of the monomeric carboxyl group. This might be expected to occur in the *cis*- and *trans*-forms, (VII) and (VIII). Calculation of the interaction of the two groups C=O and O—H in these cases, using the same data as for the dimer except that the O—H bond distance is 0.96 Å, and  $\angle \text{COH} = 110^\circ$  gives the following results (cal./g. mol.):

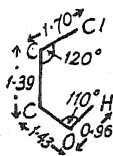


	Dipole interaction	Induction effect.	Total.
(a) <i>Cis</i> -form	—10,960	—3490	—14,450
(b) <i>Trans</i> -form	—4,100	—2930	—7,030

The difference of 7420 cal. in these totals may be taken as a measure of the stability of (VII) relative to (VIII). Using a factor of  $e^{\delta E/RT}$ , it may be estimated that at room temperatures the relative frequency of occurrence of the two forms is  $3.62 \times 10^5 : 1$ . This conforms with the complete absence of the structure (VIII) as indicated by spectroscopic analysis.<sup>21</sup>

**Benzoin.** Another molecule in which the same two groups interact is benzoin,  $\text{C}_6\text{H}_5\text{CHOH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ . Here, the interposition of the C—C bond reduces the calculated energy difference to 3530 cal./g. mol.:

	Dipole interaction.	Induction effect.	Total.
<i>Cis</i> -form	3790	515	4305
<i>Trans</i> -form	556	220	776



(IX)

This value of  $\delta E$  is of the same order as that (4800) estimated in Part II from the frequency shift between the two forms.

**o-Chlorophenol.** In treating this molecule the electron diffraction value of the C—Cl distance in chlorobenzene has been used,<sup>22</sup> and the moments  $\mu_{\text{Cl-C}} = 1.56\text{D}$ ,  $\mu_{\text{O-H}} = 1.73\text{D}$ :

	Dipole interaction.	Induction effect.	Total.
<i>Cis</i> -form	2040	468	2508
<i>Trans</i> -form	432	293	725

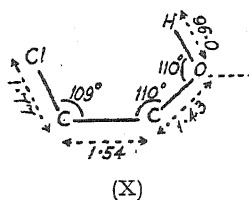
The estimated difference of 1780 cal./g. mol. is in reasonable agreement with the value of 1400–1700 cal. deduced from estimates of the relative intensities of the absorptions corresponding to the two forms of the molecule.

**o-Bromophenol.** The energy values are very near those in chlorophenol, and give an estimated energy difference of 1630 cal./g. mol.:

<sup>21</sup> Bauer and Badger, *J. Chem. Physics*, 1937, **51**, 852.

<sup>22</sup> Glasstone, *Ann. Rep. Chem. Soc.*, 1936, **33**, 76.

	Dipole interaction.	Induction effect.	Total.
<i>Cis</i> -form . . .	1820	638	2458
<i>Trans</i> -form . . .	482	350	832



**Chloral Hydrate.** It is very probable that owing to the interaction of the O—H and C—Cl groups the structure will be in or near one plane. Accordingly, the form depicted has been assumed for this system. Taking the *cis*- and *trans*-orientations as corresponding to the clamped and free forms of the O—H group, and calculating the two contributions as before :

	Dipole interaction.	Induction effect.	Total.
<i>Cis</i> -form . . .	3760	1080	4840
<i>Trans</i> -form . . .	90	430	520

It is seen that the *cis*-orientation of each OH group is stabilised by an interaction energy of about 4300 cal. which would correspond to a frequency distribution of 1700 : 1 in favour of the clamped position, or of  $2.9 \times 10^6 : 1$  as between the structure with the two hydroxyls towards the chlorines and that with them both in the opposite orientation.

Summarising these results, it is clear that simple electrostatic forces are sufficient to account for a considerable variety of interactions involving the OH group. Provided the interactions are endowed with the requisite energy their other characteristics follow, and these appear in a continuous range from the simple *cis-trans*-distribution in *o*-chlorophenol to the formation of a new molecular species of considerable stability in the case of the carboxyl dimer. There seems to be no strong practical reason for the introduction of a special mechanism of a "hydrogen bond" to account for the observed energy effects, and although the existence of a resonance contribution is an *a priori* likelihood in most cases, its magnitude would often appear to be negligible.

### Summary.

(i) Infra-red measurements on chloral hydrate in solution have shown a considerable interaction between the OH groups and the adjacent  $\text{CCl}_3$  radical. This interaction is related to the peculiar stability of the compound and similar results for analogous structures are presented.

(ii) The relation of the frequency change in the OH group between two structures and the corresponding energy difference is discussed. The unsatisfactory nature of those estimates assuming identical anharmonicity factors in the two structures is indicated.

(iii) Electrostatic energies are evaluated for interactions involving the OH group. With reasonable assumptions, these are found to account for the observed effects in a considerable variety of cases, and it is suggested that the magnitude of the resonance contribution to the stability of the "hydrogen bond" may often be negligible.

The author owes the suggestion of examining chloral hydrate in the infra-red to a discussion with Dr. T. P. Hughes. He is also indebted to the Department of Scientific and Industrial Research for a Senior Award, and to the Chemical Society for a grant.

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## THE VAPOUR PRESSURE OF OLEUM.

By F. D. MILES, H. NIBLOCK AND G. L. WILSON.

*Received 29th August, 1939.*

In addition to the vapour pressure determinations of McDavid<sup>1</sup> for oleum containing up to 40 % of pure sulphur trioxide, at temperatures between 10° and 50°, two other series of data are to be found in the literature. The first was published by Knietsch in his well-known paper of 1902<sup>2</sup> and the second was contributed to the International Critical Tables (Vol. III) by the Eastern Laboratory of Messrs. E. I. duPont. Both series cover most of the temperature range 20°-100° C. and of the concentration range 0-100 % free trioxide, but in neither case are the actual experimental results given, or the method by which the figures in the tables are derived from them. Knietsch indeed has stated that "On this account" (that mercury is attacked by pure sulphur trioxide) "the measurement was carried out in an iron apparatus by means of a manometer, which was quite accurate enough for experimental purposes." Below the title is given " $\frac{3}{4}$  vol. Oleum +  $\frac{1}{4}$  vol. Air)" from which it appears that the containing vessel was only  $\frac{3}{4}$  filled with acid, having air above the acid presumably at one atmosphere pressure. The pressures recorded are evidently the excess over about an atmosphere, but whether any deduction has been made for the increase of the air-pressure at higher temperatures, or what the temperature was at which the instrument was filled, or whether the pressure of air was exactly one atmosphere when the filling was done (most unlikely, in view of the high vapour pressure of the stronger oleum), is quite impossible to find out. Other peculiarities of this set of figures will be mentioned later.

The duPont figures cover the range of free sulphur trioxide 0.66 % and are limited to temperatures which vary between 55° (for 66.9 %) and 90° C. (for 33.3 %). The divergence between this set and Knietsch's is very wide and is not always in the same sense. Oleum of 30 %, for instance, shows 152 mm. pressure at 60° according to Knietsch; according to duPont the pressure of 31 % oleum at the same temperature is 74 mm. On the other hand, for 40 % at 75° the pressure recorded by Knietsch is 360 mm.; that given by duPont is 539.5 mm. Again, the two values are respectively, for 60 % acid at 55°, 730 mm. and 512 mm.

Redetermination was clearly necessary. Choice of methods lay between the dynamic method of boiling under various definite pressures and the static method of measuring pressures at definite temperatures. The latter was preferred, although the presence of air dissolved in the liquid is a source of error and the most stringent precautions possible must be taken on this account. It was decided therefore to synthesise the oleum by distilling pure sulphur trioxide into the bulb of the vapour pressure apparatus containing sulphuric acid (98.5 %  $\text{H}_2\text{SO}_4$ ) which had been degassed by stirring and heating *in vacuo*. By adding further portions of sulphuric acid to the oleum it was hoped to carry out several

<sup>1</sup> *J.S.C.I.*, 1924, 43, 57T.

<sup>2</sup> *Ber.*, 1902, 34, 4112.



series of determinations in succession for several varieties of oleum, but the manipulation required to admit the sulphuric acid and to exclude all air was found impracticable and each variety of oleum was made up from its components, the apparatus being cut open and sealed up again for each series of determinations.

The field of the measurements was limited on two sides. The temperature could not safely be raised above  $175^{\circ}\text{C}$ . because of the soldered joints of the air-bath, and the maximum pressure which could be recorded on the mercury manometer was 950 mm. In this field, however, lie all the data which are likely to be of any technical interest. Complete series of determinations were made for the following concentrations: 6.9 %, 12.7 %, 21.1 %, 32.3 %, 48.2 % and 64.9 %, and since the apparatus was very suitable for the redetermination of the vapour pressure of pure sulphur trioxide, this was undertaken also, the manometer being doubled for the purpose in order to record pressures of about two metres.

### Experimental.

**General.**—As  $\text{SO}_3$  attacks Hg, it was not possible to measure the vapour pressure of oleum directly on a Hg manometer. It was therefore decided to introduce a glass Bourdon gauge between the oleum and the manometer, by passing air into, or withdrawing air from, the space between the gauge and the manometer. When the needle of the gauge

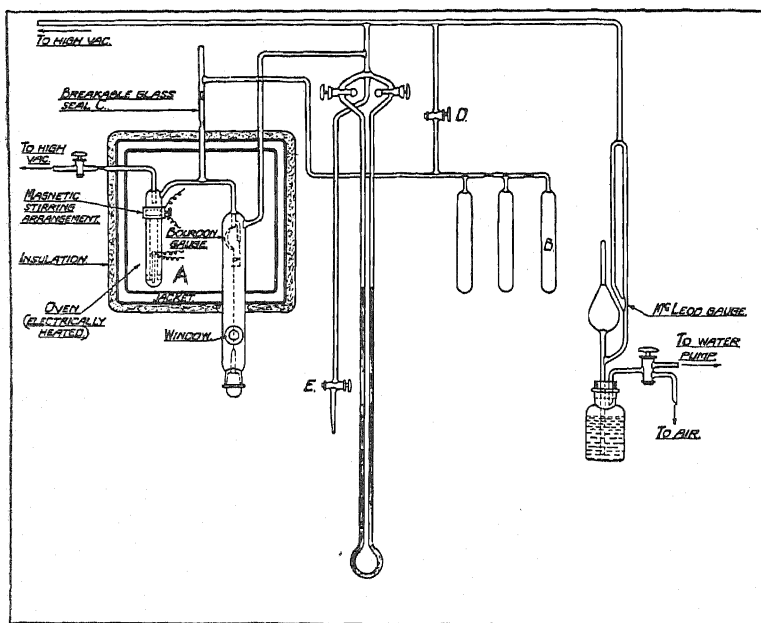


FIG. 1.

was at zero position, the vapour pressure of the oleum was the same as that indicated on the manometer.

The gauge as used for  $\text{HNO}_3$  vapour pressure determination could not be used in this case as it is not possible to make one of this kind which would withstand the very large pressure differences encountered, and at the same time be sufficiently accurate for our purpose. A modified

form of Bourdon gauge which was devised by B. S. Foord<sup>3</sup> proved to be sensitive to 0.1 mm. of Hg, and yet able to bear more than an atmosphere difference of pressure between the two sides.

A diagrammatic representation of the final set-up of the apparatus is given on Fig. 1.

The measurements were carried out in a large electrically heated air oven, heated on all six sides so as to give an even temperature throughout. A liquid bath would have given better temperature control, but no common liquid except  $\text{H}_2\text{SO}_4$  can safely be used to withstand the risk of mixing with hot  $\text{SO}_3$ ; water was considered to be out of the question.

The temperature was measured by means of thermo-couples, one in a tube which was passed under the surface of the oleum, and one fixed to the wall of the bath. Two thermo-couples were used, because it was found that there was considerable divergence between the temperature of the oleum and the surrounding air, particularly after the apparatus had been heated or cooled in order to take readings at another temperature. Readings were taken only when the temperature of the bath wall and of the oleum were the same. For greater accuracy in measurement the "cold" junctions of the thermo-couple were placed in an oil bath, the temperature of which could be read on a thermometer, and could be adjusted to give a "null" deflection on the galvanometer. Temperatures could thus be determined to less than 0.2° C.

**Method of Stirring.**—It was important that the oleum be efficiently stirred, because of the fact that trioxide tended to escape only from the surface layers when the temperature was increased, and to condense only on the surface layers when it was lowered. Thus in the first case the surface layer should have a lower concentration and therefore a lower vapour pressure than that of the remainder of the oleum. In the second, the effect should be reversed. The oleum was therefore stirred by a magnetic stirring arrangement, with an automatic make and break, such that a metal stirrer covered with platinum was pulled up by an electro magnet when the circuit was completed, and allowed to fall gently when the circuit was broken. The stirrer was not worked continuously because of the heat which resulted from the passage of an electric current through the coil of the magnet, and tended to overheat that part of the apparatus in close proximity to the coil.

**Preparation of Oleum.**—In order to free the oleum and glass apparatus from air and other adsorbed gases, the following procedure was adopted.

Concentrated  $\text{H}_2\text{SO}_4$  of known strength was weighed into the tube A (Fig. 1) and then sealed on to the rest of the apparatus, the air which was used to expand the joints in glass blowing being dried by passing through calcium chloride tubes. The glass bulb B was then weighed and a known weight of 65 % oleum introduced. This bulb was now sealed on to the apparatus, using dried air.

The oleum was then cooled down in a paste of solid  $\text{CO}_2$  and acetone, in order to reduce its vapour pressure to a very low value, and both halves of the apparatus, *i.e.* on both sides of the breakable glass seal C, were evacuated by the mechanical and Hg vapour pumps. When the pressure as shown on the McLeod gauge was fairly low (about  $10^{-2}$ ), the stopcock D was closed. The freezing mixture was now applied to the second bulb, and the bulb B heated slightly (to 40° C. or less) using a bath of concentrated sulphuric acid. When sufficient  $\text{SO}_3$  had distilled over, the bulb B was sealed off at the constriction and the weight of residual oleum found. Stopcock D was opened and any air which might now be present in the apparatus was removed by pumping, using the high vacuum system. Stopcock D was then again closed, and sulphur trioxide distilled from the second to the third bulb by cooling the third and heating the second bulb. The latter was then sealed off.

<sup>3</sup> *J. Sc. Instr.*, 1934, 11, 126.

Meanwhile the concentrated  $\text{H}_2\text{SO}_4$  in bulb A was being freed from air by connection to the diffusion pump and heating to about  $80^\circ \text{C}$ ., while being stirred intermittently by means of the magnetic stirring arrangement. The glass seal C was now broken by a metal plunger which was pulled up by a magnet and then allowed to fall on to the seal. The freezing mixture was removed from the third bulb, applied to the tube A, and distillation of  $\text{SO}_3$  carried on until sufficient was judged to have passed over into the concentrated  $\text{H}_2\text{SO}_4$  to give an oleum of the required concentration. The third bulb was then sealed off as close to the wall of the bath as possible, and after a thorough evacuation of the oleum at low temperature the bulb A was detached from the pump by sealing off close to the wall at the constriction. Much delay was caused and many runs spoiled by the cracking of the oleum bulb when the  $\text{SO}_3$ , which had been frozen in it, was melted. This could not always be prevented, but happened much less often when the melting was carried out by surrounding the bulb with  $\text{H}_2\text{SO}_4$  and manipulating in such a way that the  $\text{SO}_3$  was liquefied first at the upper surface, so that the enclosure of liquid by a solid plug above was avoided.

**Fixing the Zero of the Bourdon Gauge.**—In order to have a fine end on the moveable pointer of the gauge a short length of very fine wire was fixed to it by means of cement, and its lateral movement was observed against a similar wire attached to a rigid piece of glass rod. This movement was observed through a small low power lens. Owing to the great difficulty of fixing these wires so that they were exactly in line when the pointer was in a zero position, it was found to be more practicable to fix the wires fairly close together and then to find the pressure required to bring them into line with each other. This was done for each set of measurements by cooling the oleum to reduce its vapour pressure to as low a value as possible (about  $10^{-3}$  mm.), completely evacuating the apparatus on the other side of the gauge, and then admitting air slowly through the stopcock E to the left hand limb, which was in direct contact with one side of the Bourdon gauge, until the wires on the gauge coincided. This pressure was read off on the manometer, and subtracted from all subsequent readings.

### Measurement of Vapour Pressure.

The bath was now raised to the required temperature, the oleum being stirred now and then with the magnetic stirrer, particularly before each pressure reading. When the temperature of the oleum and of the bath walls was the same, the vapour pressure of the oleum was measured by admitting air to the left-hand limb of the manometer and one side of the Bourdon gauge through the stopcock E until the crosswires coincided. As there was a high vacuum in the right-hand limb of the manometer, the difference between the cathetometer reading of the mercury in the two limbs, less the correction, was equal to the vapour pressure of the oleum in millimetres of mercury at the measured temperature.

### Measurement of Concentration.

To determine the concentration of  $\text{SO}_3$ , the acid was weighed in single-stemmed "oleum bulbs." The weighed bulb was heated slightly in a Bunsen flame, and the open end of the capillary inserted under the surface of the oleum. When sufficient oleum had been sucked in, the end of the capillary was sealed off in a flame. Thereafter the oleum was estimated by breaking under water in a closed glass-stoppered bottle and titrating with normal sodium hydroxide solution.

From the known weight of 65 % oleum which was originally taken for each series of measurements, from the total weight of oleum and  $\text{SO}_3$  remaining in the bulbs which were removed after sealing off, and from the

weight of  $\text{H}_2\text{SO}_4$  put into the measurement bulb, the composition of the oleum synthesised could be estimated fairly closely. In Table I are given the final analytical figures, together with the compositions estimated from the weights.

TABLE I.

### Vapour Pressure of Pure Sulphur Trioxide.

It was found necessary to make minor alterations in the apparatus in order to obtain anhydrous  $\text{SO}_3$ . It is important that the trioxide be kept free from small quantities of water, as the presence of water in extremely small amounts favours the production of the "asbestos" form of  $\text{SO}_3$ , which has a higher melting-point, than the normal form melting at  $16.8^\circ\text{C}$ . and boiling at  $44.5^\circ\text{C}$ .

The concentrated oleum was introduced as before into bulb A (Fig. 2), the system evacuated through stopcock D, and  $\text{SO}_3$  distilled as before into bulb B. Both tube A and tube B were now cooled simultaneously in carbon dioxide and acetone and the whole system again evacuated, after which the first constriction was closed. Thus, the portion of the apparatus which remained was glass-sealed without stopcocks, and there was no risk of contamination of the trioxide by any products of its action on stopcock grease.

The trioxide in bulb B was now distilled in the usual fashion over  $\text{P}_2\text{O}_5$  into the bulb C, and the tube B removed by sealing at the con-

Composition from Weights taken.	Composition by Analysis.
6.65 % free $\text{SO}_3$	$\left\{ \begin{array}{l} 6.91 \text{ free } \text{SO}_3 \\ 6.89 \end{array} \right.$
13.4 known to be inaccurate	$\left\{ \begin{array}{l} 12.69 \\ 12.96 \end{array} \right.$
21.35	21.08
33.55	$\left\{ \begin{array}{l} 32.34 \\ 32.29 \end{array} \right.$
(38.50)	(38.98)
48.50	48.20
65.50	$\left\{ \begin{array}{l} 64.62 \\ 64.78 \end{array} \right.$

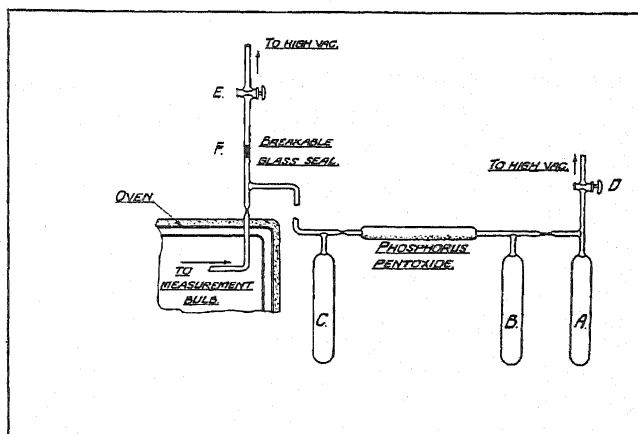


FIG. 2.

striction. Some of the trioxide in bulb C was now redistilled into the measurement bulb and the bulb C sealed off. In order to remove any air or other gas which might have been given off during these distillations, the measurement bulb and its contents were thoroughly frozen, the breakable glass seal F was broken, and the apparatus thoroughly evacuated through the stopcock E, after which the constriction close to the wall of the bath was sealed off.

It was found that the trioxide tended to volatilise and condense on the side tubes and Bourdon gauge, particularly when the temperature

of the bath was being lowered. This seemed to be due to the fact that the mass had a greater temperature-lag than the rest of the apparatus, and this caused distillation on to the colder side tubes and gauge. The latter were therefore wound with fine resistance wire held between layers of asbestos paper. During vapour pressure measurements a small electric current, sufficient to maintain the temperature *slightly* above that of the  $\text{SO}_3$ , was passed through the wire. Care was taken to see that the surface of the liquid was not overheated in this way.

TABLE II—VAPOUR PRESSURE OF OLEUM.

6.89 % $\text{SO}_3$ .		12.7 % $\text{SO}_3$ .		21.08 % $\text{SO}_3$ .		32.3 % $\text{SO}_3$ .		48.2 % $\text{SO}_3$ .		64.7 % $\text{SO}_3$ .	
<i>t</i> (°C.).	<i>p</i> (mm. Hg).	<i>t</i> (°C.).	<i>p</i> (mm. Hg).	<i>t</i> (°C.).	<i>p</i> (mm. Hg).	<i>t</i> (°C.).	<i>p</i> (mm. Hg).	<i>t</i> (°C.).	<i>p</i> (mm. Hg).	<i>t</i> (°C.).	<i>p</i> (mm. Hg).
20	2.1	28	2.5	17.5	2.3	18.5	3.7	14.5	15.3	1.5	25.4
28	2.9	34	3.7	20	2.9	20	5.2	18	21.5	8.2	43.8
34.3	3.3	43	4.7	47	9.5	34	10.7	18.5	21.6	9.3	54.2
37	3.7	58	12.1	61	23.7	36	12.9	24.5	28.0	11.4	61.5
42	4.4	59.5	12.7	81.2	70.6	38	15.9	27.5	36.4	15	80.1
43	4.5	60	13.5	93.0	109.1	41	18.8	32	47.7	18	92.2
46	5.1	62	14.7	101.2	150.7	44.5	22.1	39	70.2	19.8	107.0
55	7.4	65	16.0	117	269.3	45	24.0	41	78.3	23.4	131.1
57	7.8	70	21.3	127.5	410.0	49	29.8	44	96.1	25	150.8
60	8.8	71.5	22.2	132	520.0	52	37.2	46	106.9	31.5	210.9
61	9.2	81.5	29.0	137	667.0	55	43.9	47	118.9	34	241.5
64	10.0	87	44.7	140.5	790.0	61	54.8	51	135.5	35.3	263.1
66	10.8	98	64.9	143	901.3	70	98.1	54	169.3	42.6	389.2
67	11.1	99	71.5	—	—	77	138.1	58.5	204.0	46	445.2
80	16.3	100	73.8	—	—	79	163.6	62	257.4	52	594.6
81	17.1	104	84.7	—	—	86	234.3	65	285.3	52.8	619.7
85	19.8	107.5	93.2	—	—	91	290.5	73	418.2	55.5	706.9
94	26.6	108.5	97.6	—	—	92	311.7	76	499.2	59.6	832.7
100	32.3	112.5	117.2	—	—	92.5	318.1	82.3	663.6	60	862.4
105	39.2	120	153.2	—	—	99	406.0	85	741.0	60.8	873.4
108	46.1	125	187.4	—	—	102	474.7	85.5	760.0	61.1	890.7
109	47.0	126	199.0	—	—	108	603.7	89	871.0	—	—
118	68.0	129	225.6	—	—	112	737.5	—	—	—	—
131	114.0	137	286.8	—	—	113.5	814.5	—	—	—	—
144	179.1	140	319.6	—	—	115	899.5	—	—	—	—
149	217.3	141	336.0	—	—	117	931.5	—	—	—	—
164	375.3	142	346.9	—	—	—	—	—	—	—	—
167	417.4	148	420.6	—	—	—	—	—	—	—	—
170	465.1	151.7	480.0	—	—	—	—	—	—	—	—
—	—	152	484.0	—	—	—	—	—	—	—	—
—	—	153.7	607.6	—	—	—	—	—	—	—	—
—	—	166	756.6	—	—	—	—	—	—	—	—
—	—	172	926.6	—	—	—	—	—	—	—	—

In order to get readings of pressures higher than one atmosphere, the right-hand limb of the U-tube manometer was filled with air at atmospheric temperature and pressure before being closed instead of being evacuated. The vapour pressure of the  $\text{SO}_3$  was therefore equal to the pressure of this air plus the difference of mercury levels. The pressure in the closed limb was easily calculated from the change in volume as it was compressed. A thermometer was strapped to the tube and read to make sure that no significant change of temperature took place during this compression. It was not considered advisable to go higher than about  $2\frac{1}{2}$  atmospheres.

## Results.

All the readings of the vapour pressures of the six different concentrations of oleum with the temperatures at which they were made are included in Table II.

Table III gives the results for pure sulphur trioxide.

TABLE III.—VAPOUR PRESSURE OF SULPHUR TRIOXIDE.

## Graphical Treatment.

The oleum data were plotted on squared paper (to the scale of 1 cm.  $\equiv$  4° C.  $\equiv$  20 mm. Hg) and a smooth curve was drawn through each set of points with a flexible celluloid curve-tracer held by steel clamps.

These six curves gave the data exactly as they were obtained (in the form of  $p-t$  curves, the composition being constant for

practical purposes each curve), but for the curves must be spaced at regular intervals and it is preferable to plot for fixed values of the temperature.

The complete series of isothermal ( $p-t$ ) curves for intervals of 10° C. is reproduced in Fig. 3. They were obtained for the most part from the original  $p-t$  curves, simply by reading off the pressures corresponding to even decades of temperature, for each sulphur trioxide concentration, and then replotting as curves of constant temperature. This was not sufficient, however, for the region of higher pressures, because the  $p-t$  curves are there nearly vertical, and the ordinates of temperature on which readings are required rarely intersect them. Two separate  $t-c$  curves were therefore drawn again for pressures of 900 and 650 mm. From these were taken the values used to complete the higher region of Fig. 3. There is no reason to believe that the points obtained in this way are less trustworthy than the original points.

To this procedure one exception had to be made. When the logarithmic plots ( $\log_{10} p - 1/T$ ; see below) were inspected it was found that each set lay close to a straight or simple curve, except that for 21 % free trioxide which departed appreciably from the straight line of closest fit without falling as a whole as any other curve of single inflection. The result of this irregularity was that the final smoothed vapour pressures, when tested by plotting as logarithmic curves, showed this defect not only for 20 % but for other concentrations in that neighbourhood. It was therefore considered best in deriving the smoothed values to substitute, for the actual experimental pressure values for 21 % (but only in this case), those read from the logarithmic line of closest fit. This rather arbitrary procedure is largely justified by the concordance it introduces into the smoothed values at and near 20 % free trioxide.

There is a certain doubt about the lower parts of the isotherms for 160° and 170°. Neither curve can pass through the origin, on account of the appreciable vapour pressure of 100 % sulphuric acid at these

Readings with Ordinary Manometer.		Readings with Pressure Manometer.	
$t$ (°C.).	$p$ (mm. Hg.).	$t$ (°C.).	$p$ (mm. Hg.).
17.5	148	47.1	858
21	193	49.7	989
25.3	259	49.8	989
27.2	293	50.0	1007
28.1	307	50.5	1035
32.4	398	54.5	1241
36.8	504	55	1284
37.5	526	57.6	1433
39.5	581	58.1	1486
41.0	631	61.5	1703
43.0	702	62.0	1743
43.5	719	—	—
45.1	777	—	—
47.0	853	—	—
48.0	893	—	—

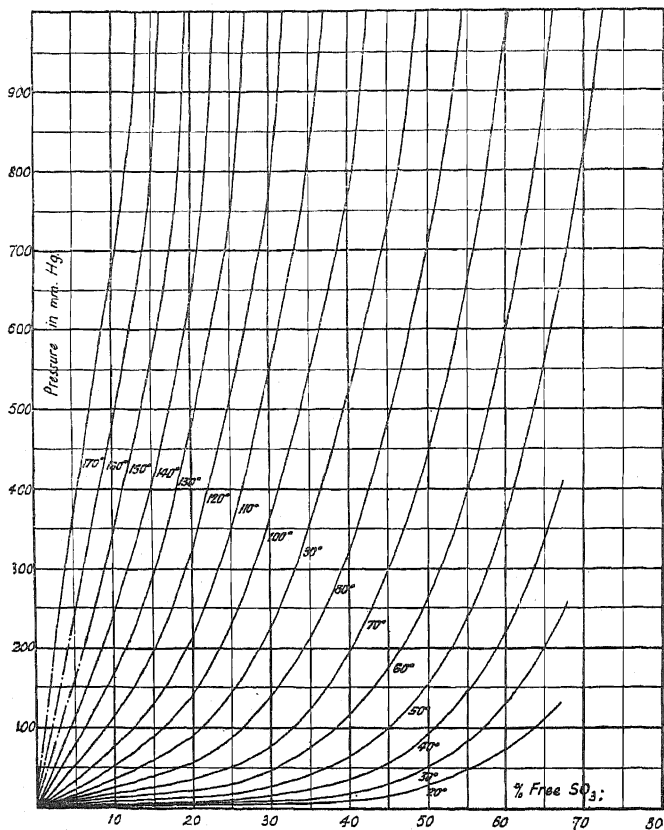


FIG. 3.—Smoothed values of vapour pressure of oleum.

TABLE IV.—VAPOUR PRESSURE OF OLEUM, AT INTERVALS OF 10° C. AND 5 % FREE SO<sub>3</sub>. (READINGS FROM *p-c* CURVES (FIG. 3).)

[illegible]

temperatures. These pressures have not been directly measured, but extrapolation of the results of Thomas and Barker<sup>4</sup> leads to the rough values for the total pressures of 7.0, 12.5 and 21.0 mm. at 150°, 160° and 170° C. respectively.

### Heats of Vaporisation.

Fig. 4 shows the experimental data plotted as  $\log_{10} p$  against  $1/T$ .

They should fall on straight lines, the slopes of which are  $Q/2.303R$  ( $Q$  being the molecular heat of vaporisation) so that  $Q$  can be found in calories, for each line, as  $4.573 \times$  the determined slope of the line.

These plots were made to the largest practicable scale on paper (40 × 70 cm.) and the locations of the best-fitting straight lines were found by a convenient approximate graphical method of Least Squares. On the whole the fit is fairly good, but the two weakest oleums show, for the lower range of pressure, a departure from the straight line in the sense of excessive pressure which is difficult to account for. It is found only when both temperature and concentration are at their lowest and shows a certain gradation with concentration. There seems to be no source of experimental error from which a graded effect of this kind could arise and it seems more likely that the two logarithmic lines for 6.9 and 12.8 % are actually curved, in correspondence with a decrease in the latent heat of evaporation which occurs in these two cases, to a greater or less extent, as the temperature falls. Since, however, the readings at higher pressures were more important as results and were also proportionately less liable to the effect of some constant error—as, for instance, inaccuracy of the gauge—it was decided that in fixing the positions of the straight lines all readings of pressures below 12 mm. should be discarded.

The molar latent heats of vaporisation of the trioxide from the several varieties of oleum, including the pure trioxide, are as follows: 6.4 % free trioxide—12,100 cal.; 12.7 %—11,300 cal.; 21.1 %—12,190 cal.; 32.3 %—12,500 cal.; 48.2 %—11,190 cal.; 64.7 %—10,240 cal.; trioxide—10,485 cal. There is a certain variation in the figures, visible in Fig. 4 as a slight lack of parallelism of the lines, which is by no means necessarily due entirely to experimental error.

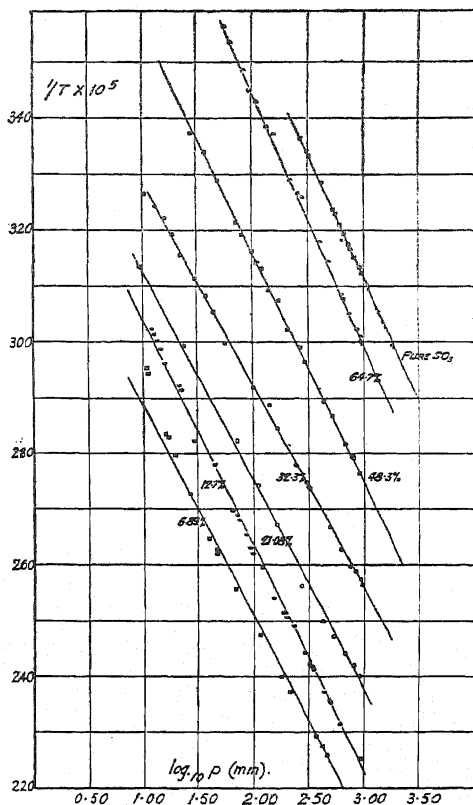


FIG. 4.—Vapour pressures of oleum and sulphur trioxide; logarithmic curves.

<sup>4</sup> J.C.S., 1925, 127, 2820.



### Discussion.

It has already been pointed out that the existing sets of data agree very badly with each other. The new set agrees well with none of them. The figures cover a wider field than any of the old.

The data of McDavidd and Chadwick are only for pressures below 60 mm. On the whole they are lower, but the difference is not regular; at 40°, 50° and 90° they agree well with the new data but diverge widely at the intermediate temperatures.

Knietsch's results are higher than ours—sometimes more than twice as high. In the Introduction we pointed out that he measured his vapour pressures in presence of air and seems to have made no allowance for the expansion of this air on heating. If we assume that the air pressure was exactly one atmosphere when the manometer was filled and the temperature 20°, allowance can be made. It thus appears that although the correction cannot be more than a rough one, and actually results in some instances in a negative vapour pressure, the agreement between the values obtained in this way and our own is better than with any other set.

The duPont values agree with none of the others, least of all with our own, which they exceed occasionally by more than 100 %. It is difficult to account for such large differences without knowing how the results were obtained or correlated. When plotted they give regular  $p-t$  curves. The  $\log p-1/T$  graphs are straight lines and nearly all the points fall exactly on them. Indeed, points for the pressures under 1 mm. which are recorded in the duPont table also coincide exactly with the lines. This could hardly happen with such low pressures determined by any method generally applicable over the whole range of the measurements unless some smoothing had been carried out, and it is possible that the logarithmic lines themselves have been used to smooth all the results. From the slopes of these lines the latent heats of vaporisation appear to increase in a regular way from about 10,000 cal. for 60 % to about 17,000 cal. for 10 %. Such values are not impossible; the duPont data bear no evidence of inconsistency.

There is one way, however, in which vapour pressure measurements may be tested against other experimental results.

TABLE V.—BOILING-POINTS OF OLEUM.

% Free SO <sub>3</sub> .	Directly Determined by Knietsch (°C.).	From Vapour Pressure Curves (Ardeer).	Extrapolated from duPont Data.
3.6	212	—	—
9.6	170	175	137
26.2	125	128	115
42.8	92	94.5	75
63.2	60	50	53

The boiling points of certain oleums were found directly by Knietsch. In Table V the experimental and the deduced values are compared. Those derived from our own results were read from the curves of Fig. 3 directly, those from duPont's had necessarily to be found by extra polation, since their measurements were limited to 500 mm. For this purpose the  $\log p-1/T$  curves of their data were used—a legitimate procedure since the data fit them closely.

Knietsch's figures and our own agree very well, but these derived from the duPont data depart so widely that the method of derivation

can account only for a small fraction of the difference. Our data, therefore, withstand the few tests that can be put to them.

The latent heats of vaporisation are somewhat unexpected. For sulphur trioxide the most trustworthy values are probably those obtained from vapour pressure data by Berthoud,<sup>5</sup> who found 10,580 cal. for the whole interval 25-44° C., and by Smits,<sup>6</sup> who found 10,100 cal. between 17° and 90° C. With these our figure of 10,480 cal. is in fair agreement, but those for the oleums tend to rise as the percentage of free trioxide falls, and to reach a maximum at about 30 % of pure trioxide. A rise is to be expected, because the latent heat of the pure trioxide must be less than that of very dilute oleum by the heat of mixing trioxide with great excess of sulphuric acid. It is doubtful how great this heat of dilution actually is. From Knietsch's investigation of the heats of dilution of various oleums in large excess of water, Porter<sup>7</sup> obtains certain figures ( $k$ ) representing the heat in calories liberated when 1 g. of water is mixed with  $m$  g. of sulphur trioxide to form a certain oleum. The differential heat of mixing—*i.e.* the heat evolved when 1 g. of trioxide is mixed with a very large amount of oleum, must be  $dk/dm$  and for the quantity the figures give approximately 1500 cal. for 73 % and 3000 cal. for 18 % oleum. There is, however, no sure ground here for comparison, for Porter has pointed out that Knietsch's vapour pressure measurements are inconsistent with his calorimetric data and indicate the heat of dilution of trioxide in any proportion of sulphuric acid to be zero. A redetermination of these thermal values by direct methods would be useful, and is being made.

The vapour pressures have one peculiarity which is not altogether unexpected. If the isothermal curves of Fig. 3 representing change of pressure with concentration are examined, it will be seen that they cannot pass through the corresponding points for the pure trioxide without undergoing a marked change of curvature in the region 70-100 % free  $\text{SO}_3$ . The isothermals for 20°, 30°, 40° and 50° at least, must be S-shaped. This fact is interesting, and is quite in accordance with what we know of the associated nature of liquid sulphur trioxide; its very high specific heat, for instance, or its high value of Trouton's constant. On account of the association, the vapour pressure of the pure substance is lower than if its molecular condition were simple. When sulphuric acid is added the complex molecules are broken down, and the effect of diluting the trioxide with a non-volatile liquid, which would normally be to depress the vapour pressure sharply, is delayed by the increase in the activity of the trioxide. As more acid is added simple molecules of trioxide become more numerous and dilution causes the vapour pressure to fall in the usual way.

### Summary.

The vapour pressures of oleum have been determined over a field which is limited generally by a concentration of 65 % free trioxide, and a pressure of 950 mm. and at particular points by a temperature of 170° C. The results agree with none of the published sets of oleum vapour pressures, but nevertheless appear to be reliable, and are in agreement with indirect estimates of the vapour pressure from certain other data. Some peculiar

<sup>5</sup> *Helv. Chim. Acta*, 1922, 5, 513.

<sup>6</sup> *J. Chem. Soc.*, 1926, 1108.

<sup>7</sup> *Trans. Faraday Soc.*, 1917-18, 13, 392.

features of the vapour pressure curves are discussed. The vapour pressures of sulphur trioxide have been redetermined from 17° to 62° C.

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*The Nobel Laboratories,  
Ardeer.*

## THE PARTIAL PRESSURES OF NITRIC ACID-WATER MIXTURES FROM 0° — 20° C.

BY G. L. WILSON AND F. D. MILES.

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These measurements were carried out because of two observations made in the course of experiments on the nitration of cellulose in nitric acid vapour.

The first was that the extensive series of vapour pressures collected and recalculated by Taylor<sup>1</sup> for nitric acid-water mixtures were not in agreement with two later series by Berl and Saenger<sup>2</sup> and Klemenc and Rupp.<sup>3</sup> The last two researches deal mainly only with 100 % nitric acid and although they agree with one another, they disagree with the older figures collected by Taylor. For instance, Klemenc and Rupp give 31 mm. at 12.5° whereas Taylor's value is 30 mm. at 15°.

For the total vapour pressure over nitric acid of 82 % by weight Klemenc and Rupp give 6.9 mm. at 0° and 23.4 mm. at 25° compared with 3.1 mm. and 15.5 mm. from Taylor's figures for the same temperatures; and for 71 % acid—2.2 mm. at 12.5° compared with 4.6 mm. according to Taylor.

The second observation was that dew was formed in an apparatus containing the vapours of nitric acid and water, at a pressure of about 5.9 mm. at 20° C., whereas the lowest total pressure of any nitric acid-water mixture at 20° given in Taylor's figures was 6.4 mm. (for a composition of about 60 %-65 %). To have accurate figures for both the composition and the pressure of the vapours is important in many industrial problems.

A static method of measuring the vapour pressure was preferred to a dynamic one as capable of greater accuracy. The total pressure of the liquid was found, some of it was then distilled and the distillate analysed. The two difficulties with nitric acid were its corrosive action and its liability to decomposition (colouring).

A special apparatus was devised for the measurements.

### Experimental.

For purposes of our own work the pressures at 20° only were necessary. From these, calculated pressures for the other temperatures were derived, and a table constructed with a range of 0-20° and 50-100 % nitric acid. A few experiments at 0° were carried out to compare the results with the values calculated for that temperature.

<sup>1</sup> *Ind. Eng. Chem.*, 1925, **17**, 633.

<sup>2</sup> *Monatshefte*, 1929, **53-54**, 1042.

<sup>3</sup> *Z. anorg. Chem.*, 1930, **194**, 59.

**Material.**—The nitric acid was prepared from 70 % A.R.  $\text{HNO}_3$  by distillation with  $\text{H}_2\text{SO}_4$  under reduced pressure. An all-glass apparatus, as shown in Fig. 1, was used and the one stopcock was moistened with phosphoric acid lubricant. The ground-joint was sealed with  $\text{H}_2\text{SO}_4$ . Distillations were conducted at room temperature and the vapour condensed at  $-80^\circ$ ; in this way a colourless acid was obtained, the strength of which was estimated by titration. Several distillations were necessary to reach 100 % nitric acid. In the last distillation  $\text{H}_2\text{SO}_4$  was omitted in case slight splashing occurred, but in any event the acid was tested for sulphates. The nitrous acid content was practically nil.

**Analysis.**—When higher concentrations of acid were analysed some acid was introduced into a bulb by warming and then cooling it. After sealing off, the bulb was weighed and then broken under water and the solution titrated with methyl orange as indicator.

With concentrations of 99.5–100 % the titration method is not likely to be as sensitive as could be desired. The density was therefore determined. Now the density cannot well be used as an absolute measure of

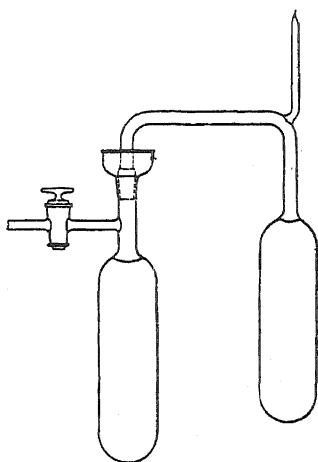


FIG. 1.

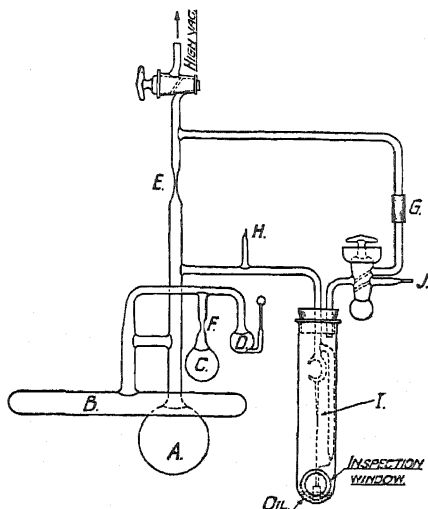


FIG. 2.

the purity, but if the curve connecting this quantity with the concentration (by titration) is drawn for a range of compositions the density forms a useful check on the concentration of any one acid. The average of all the titrations is, however, in effect the absolute standard.

**Apparatus.**—The apparatus is illustrated diagrammatically in Fig. 2. It embodied a Bourdon spoon gauge of the usual type which could be read to 0.10 mm. The remainder of the diagram explains itself.

### Procedure.

About 100 c.c. of acid of requisite strength was placed in A and frozen by means of solid  $\text{CO}_2$  in acetone. The apparatus was then evacuated. The gauge and the tube were connected during the evacuation because the gauge would fracture with any pressure difference higher than about 10 cm. of Hg between the two sides, but when the vacuum was more complete it was shut off.

The dissolved air present in the acid was withdrawn by repeated freezing and melting until a good vacuum was registered by a McLeod gauge, when the acid was frozen. It was also helpful to distil some acid

into B and back again. The apparatus was then ready to seal off at E. As a preliminary step the glass around the seals E and F was heated to drive off gas absorbed on it. After the pump had dealt with this the seal was made at E, the flexible rubber joint G allowing the necessary movement. G was detached and the apparatus could be removed to a thermostat. Firstly, however, the acid was poured over into B by tilting. (The oil used in I to steady the pointer is of such viscosity that it does not flow easily.)

The apparatus throughout the experiment was clamped to an iron rod which ran at right angles to the plane of the sketch and when in the thermostat was used as an axle about which to rock the tube so that the acid could be well mixed. A and B were in the thermostat while C, D and I hung over the front. No distillation into C, D or I took place, since the room temperature was higher than that of the thermostat (20° C.) in which a cooling-coil was fitted. In two instances when this may not have been true the results, although given, have been ignored. Arranged in this way, the apparatus was rocked for some time and then the bulb C was cooled and about 1 c.c. of acid collected. This bulb was sealed off at F and with it was removed the last trace of air or other gases. It was important that the tubing surrounding F should have previously been heated to remove absorbed gas.

The total pressure of nitric acid and water vapour was then read in the following way: G was firstly connected to a mercury-filled manometer of which the vacuum on one side was checked by a McLeod gauge. The connection between G and the U-tube also contained a tap which could be used to admit dry air or "vacuum" at will. By opening this tap and setting up a suitable pressure the pointer of the Bourdon gauge, to which a fine wire was fixed, was brought between the two fixed points also formed by fine wires. The two fixed wires lay in the plane of movement of the pointer and when observed through a microscope all three were therefore in focus. The position of the pointer relative to the fixed points could then be noted on the eyepiece scale and the difference in pressure between the bulb and the manometer could be found by interpolation after a preliminary calibration of the gauge. In each case several readings were made and the mean accepted as the total pressure of the nitric acid and water vapours. Although the readings were taken sometimes with an interval of 16 hours between, they were always found to agree within one, or at most two parts per hundred.

The next procedure was to estimate the fractional partial pressures. Some of the mixed vapours were condensed by cooling D while the apparatus was shaking. About 1-2 c.c. of liquid was condensed over a period of  $\frac{1}{2}$ -1 hour and the degree of cooling just necessary for this was applied. When the required amount of acid had collected H was scratched with a glass-knife and connected to J by a rubber connection containing a T-piece with a tap. After connecting up and opening J the tip of H was broken off inside the connection, and air allowed to enter. The distillate was forced up into the small tube attached to D.

The small bulb, really a miniature Regnault bottle, had been standardised with water to the constriction before sealing on and the density of the acid was determined in it. The bulb was afterwards broken under water and the acid titrated. The weight of the empty bulb was obtained from the fragments of glass collected in a fused glass filter. The weighings of these small objects were all carried out on an assay balance to 0.1 mg.

### Composition as shown by Density and Titration.

Mellor<sup>4</sup> quotes statements to the effect that 100 % nitric acid is unstable above — 40°. Our experience is in accordance with this. The acid,

<sup>4</sup> *Treatise on Inorganic and Theoretical Chemistry*, vol. 8.

however, could be kept for about a day at  $0^{\circ}$  and took an hour or two to develop more than a faint colouration at  $20^{\circ}$ . Below 99.5 % the decomposition is slower and 70 % acid is fairly stable if kept in the dark, preferably in full bottles. Probably the decomposition, as Velej and Manley suggested, takes place more readily in the vapour state. The nitrogen peroxide formed is very soluble in concentrated nitric acid and it was found better to concentrate colourless 70 % acid in several distillations at low temperature than to attempt to decolourise and use the plant 96 % acid. In our experience, to decolourise acid satisfactorily by blowing air through it the strength must be 88 % or less, for at such concentration the peroxide is appreciably less soluble.

The distillates from the more concentrated acids being vapourised at  $20^{\circ}$  were invariably more or less coloured, the colouration being at the most about the same as that of

N./1000 iodine solution. The effect of this decomposition on the results must be considered. As previously stated, the density was measured in the first place to check results by titration. With distillates above 99.5 %, however, it was found that the concentration by density read from our own density-titration curve no longer checked with the concentration by titration. This is shown in Fig. 3 where the figures available for the

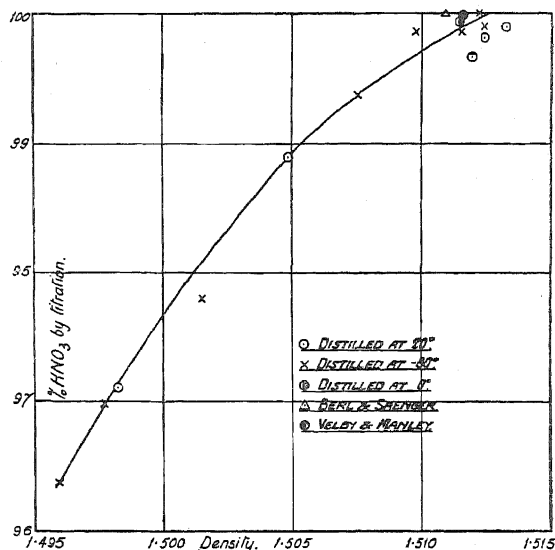


FIG. 3.

TABLE I.—ESTIMATED ERROR IN ANALYSIS DUE TO DECOMPOSITION OF NITRIC ACID IN DISTILLATES. .5 % NO<sub>2</sub> FORMED.

	No decomposition.	Decomposition according to	
		Equation (a).	Equation (b).
Titration . . .	97.33	97.29	97.40
Density . . .	97.33	97.81	97.93

density of the more concentrated solutions of nitric acid are compared with the concentration by titration.

Suppose that the decomposition occurred according to equation (a)  $2\text{HNO}_3 = \text{H}_2\text{O} + \text{NO} + \text{NO}_2 + \text{O}_2$ , or (b)  $4\text{HNO}_3 = 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$ , and that it oc-

curred during the distillation so that the total pressure reading was unaffected.

Then using the figures of Klemenc and Rupp<sup>3</sup> for the densities of mixtures of pure nitric acid with nitrogen peroxide, calculations could be made of the effect of decomposition on the titration and density. If 0.5 % by weight of peroxide were formed in a distillate by decomposition and this was not allowed for in the analytical calculations, the two methods

of estimation would give different results. Table I shows the figures which titration and density determinations would give and the results, if there were no decomposition, for the distillate from 81.2 % acid.

Of the points in Fig. 3 which lie above 99.5 %, those marked by "X," and representing values obtained directly from a supply of acid distilled at  $-80^{\circ}$ , are closer to the extrapolation of the curve obtained for pure acid at lower concentrations than those represented by "O." The latter points were distillates from determination of partial pressures and were coloured. There is one point from a distillate formed at  $0^{\circ}$  and it also lies near the curve, because the acid in this case also was only slightly coloured.

The graph shows that the density method gives a high result when there has been some decomposition, while the titration method gives a slightly too low result. Interpreting the discrepancy of 0.2 % as due to dissolved  $\text{NO}_2$ , the concentration of  $\text{NO}_2$  can be estimated from Table I as 0.2 %, and hence the error in the titration method is only  $-0.02\%$  or  $-0.03\%$  according to the equation.

Apart from providing this estimate of the possible error caused by colour in the distillate the concentration by density was not used with coloured solutions and the titration method alone provided the measure of the nitric acid concentration.

### Experimental Results.

The measurements at  $20^{\circ}$  are contained in Table II, and when plotted on squared paper satisfactory curves can be drawn through them without much difficulty (Graph 1). The composition of the original acid was used

TABLE II.—VAPOUR PRESSURE MEASUREMENTS OF NITRIC ACID-WATER MIXTURES AT  $20^{\circ}$ .

Composition by Weight.			Distillate Molecular Compositions.	Vapour Pressure (mm. Mercury).			Remarks.
Original Nitric Acid %.	Residual Nitric Acid %.	Distilled Nitric Acid %.		Total.	$\text{HNO}_3$ .	$\text{H}_2\text{O}$ .	
49.80	50.05	13.88	4.40	8.1	0.355	7.75	Contained air
—	59.53	40.70	16.40	7.7	—	—	
50.00	60.24	40.91	16.51	5.8	0.95	4.85	
69.64	69.60	77.76	49.96	5.8	2.90	2.90	Distilled at $0^{\circ}$
—	69.68	77.54	49.65	5.8	2.88	2.92	
69.80	—	—	—	5.95	—	—	
76.62	—	92.48	77.84	8.82	6.87	1.95	Fractionation *
78.80	78.50	94.59	83.34	11.5	9.58	1.92	
79.60	—	97.10	90.55	10.81	9.79	1.02	
81.60	—	97.51	91.80	13.6	12.49	1.11	Fractionation *
82.02	81.82	98.36	94.47	13.9	13.13	0.77	
86.13	—	98.90	96.25	19.05	18.34	0.71	
89.85	89.58	99.45	98.07	26.2	25.70	0.50	Not reliable
91.45	—	99.66	98.80	29.55	29.11	0.35	
91.81	91.10	99.65	98.77	30.3	29.94	0.37	
94.49	—	99.81	99.33	36.32	36.08	0.24	
96.58	96.37	99.92	99.73	41.7	41.59	0.11	
97.43	97.00	99.75	99.17	41.7	—	—	
99.78	99.75	—	—	47.8	—	—	
99.90	99.90	—	—	47.9	—	—	
99.80	—	—	—	47.8	—	—	

\* These were done during cold weather and it is suspected that the room temperature may have fallen below  $20^{\circ}$ .

in plotting the results, since the change of composition was small. The experiments which were carried out at 0° are shown in Table III where the pressures given in brackets are calculated, in the manner shown later, from Graph 1.

TABLE III.—VAPOUR PRESSURE MEASUREMENTS OF NITRIC ACID-WATER MIXTURES AT 0°.

Vapour pressures in brackets are read from curves calculated from the 20° readings (see Table V).

Composition by Weight.			Distillate Molecular Composition.	Vapour Pressure (mm. Mercury).			Remarks.
Original Acid.	Residual Acid.	Distillate		Total.	HNO <sub>3</sub> .	H <sub>2</sub> O.	
69.80	—	79.27	52.21	1.60 (1.39)	0.835 (0.74)	0.765 (0.65)	
69.90	69.39	80.19	53.65	1.55 (1.37)	0.83 (0.74)	0.72 (0.63)	
76.62	—	—	—	2.42 (2.30)	—	—	Distilled at 20°
79.60	—	—	—	2.60 (3.04)	—	—	Distilled at 20°
81.60	—	—	—	3.70 (3.70)	—	—	Distilled at 20°
83.44	—	98.74	98.74	4.50 (4.49)	4.31 (4.30)	0.19 (0.19)	
91.45	—	99.93	99.76	8.39 (8.76)	8.37 (8.70)	0.02 (0.06)	
99.80	—	—	—	14.5	—	—	Distilled at 20°

### Calculation of Vapour Pressures at other Temperatures.

The vapour pressures were required over a range of 0-20°. The values at other temperatures than 20° can be calculated by using Kirchhoff's equation—

$$\frac{dQ}{dN} = -2.30 RT^2 \frac{d}{dT} \left( \log \frac{P_0}{P} \right),$$

where  $\frac{dQ}{dN}$  is the differential heat of mixing per mol. of a component.

$P_0$  = the vapour pressure of a pure component at  $T^\circ$  and

$P$  = the partial pressure of the component in the mixture at  $T^\circ$ .

For the temperature difference  $-20^\circ$  to  $0^\circ$  it will be sufficient to take

$$\frac{dQ}{dN} = \frac{-2.30 \times 2 \times (283)^2}{20} \left\{ \log \left( \frac{P_0}{P} \right)_{20^\circ} - \log \left( \frac{P_0}{P} \right)_{0^\circ} \right\}.$$

Of the terms contained in Kirchhoff's equation the values of  $P_0$  (nitric acid) were calculated according to the equation

$$\log P = A - \frac{L}{2.30RT}$$

where  $L$  = latent heat of nitric acid,  $R$  = gas constant,  $A$  = an unknown constant,  $T$  = absolute temperature,  $P$  = vapour pressure at temperature  $T$ .

The constant  $A$  and the latent heat were calculated from the measured vapour pressures of 100 % nitric acid at  $0^\circ$  and  $20^\circ$  and the intermediate



pressures at 5°, 10° and 15° could be calculated from them. The latent heat from the vapour pressure measurements, using the approximate formula above, was 9450 cal. per mol. while Berthelot's value (the only one in the literature) is 7250 cal. In view of this disagreement the latent

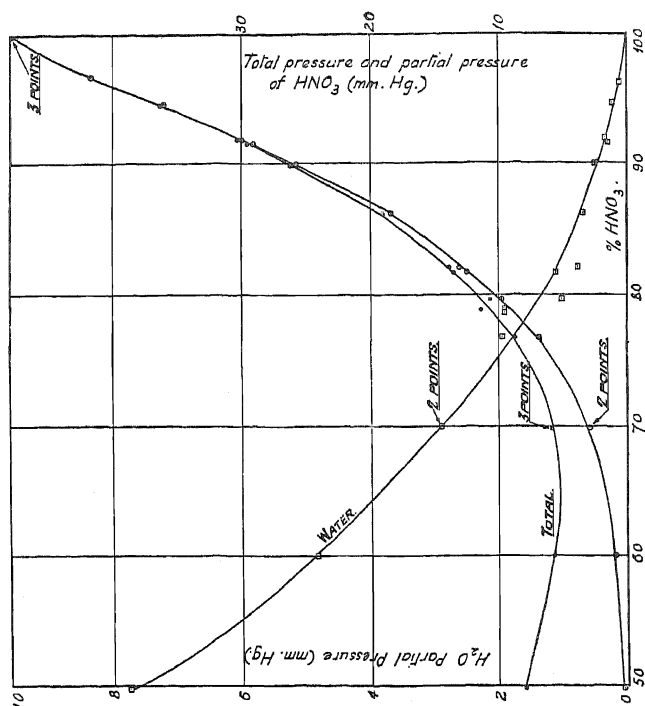


FIG. 4.—Partial pressures of aqueous nitric acid at 20° C.

heat of nitric acid was redetermined by a method which it is hoped to describe in full in connection with similar work in sulphur trioxide and oleum. Electrical heating was used in such a way that the rates of supply or electrical energy and of vaporisation could be balanced, so that the distillation was isothermal and the transference of heat between the distillation bulb and the calorimeter was almost negligible.

TABLE IV.—HEAT OF ADDITION OF 1 MOL. OF NITRIC ACID OR WATER TO A LARGE QUANTITY OF ACID OF THE STATED COMPOSITION AT 20°.

Composition % Nitric Acid.	Nitric Acid Cals. Per Mol.	Water Cals. Per Mol.
90	160	3140
80	860	2355
70	1760	1550
60	2680	750
50	3670	100(?)

The heat of vaporisation of nitric acid (99.91 %) at 20° was thus found to be 9415, and 9436 cal./g. mol. in two determinations, in good agreement with the figure obtained from the vapour pressure curves.

The values for  $P_0$  (water) are accurately known.

The differential heats of solution of nitric acid and water in nitric acids of various strengths

had been determined in the course of other work which will be reported later. They are given in Table IV. The one result which is questioned is obtained by a rather hazardous extrapolation, but the heat is known to be small and the effect on the vapour pressure will be unimportant.

In this way, all the other terms of Kirchhoff's equation,  $P_0$  (or  $P_5$ ,  $P_{10}$ ,  $P_{15}$ ) can be calculated. Table V shows the values of the partial

TABLE V.—PARTIAL VAPOUR PRESSURES OF NITRIC ACID-WATER MIXTURES.

Temperature.	Constituent.	Composition of Acid (by Weight).					
		50 %.	50 %.	70 %.	80 %.	90 %.	100 %.
0°	Water	1.97	1.19	0.617	0.266	0.083	—
	Nitric acid	0.095	0.195	0.76	2.89	7.81	14.7
	Total	2.06	1.39	1.38	3.15	7.89	14.7
5°	Water	2.80	1.73	0.92	0.409	0.132	—
	Nitric acid	0.146	0.292	1.10	4.07	10.74	20.1
	Total	2.95	2.02	2.02	4.48	10.87	20.1
10°	Water	3.95	2.49	1.36	0.619	0.203	—
	Nitric acid	0.222	0.428	1.57	5.63	14.55	27.1
	Total	4.17	2.92	2.93	6.25	14.75	27.1
15°	Water	5.48	3.52	1.97	0.92	0.309	—
	Nitric acid	0.332	0.62	2.20	7.72	19.54	36.2
	Total	5.81	4.14	4.17	8.64	19.85	36.2
20°	Water	7.53	4.93	2.83	1.35	0.46	—
	Nitric acid	0.49	0.89	3.08	10.49	26.03	48.0
	Total	8.02	5.82	5.91	11.84	26.49	48.0

pressures of nitric acid and water at 20° taken from the smoothed curve, and the values at 0°, 5°, 10° and 15° calculated from them as described above. The agreement of the observed readings at 0° and the calculated ones is satisfactory (see Table III) and reassures us that no appreciable error is introduced by the approximations of the Kirchhoff equation.

The difference between the new measurements and the older ones is quite considerable. Thus the distillates from 60, 70, 80 and 90 % nitric acid according to the older results have the respective compositions 34, 71.9, 92.1 and 98.95 %, while according to the new ones they are 38.9, 79.1, 96.5 and 99.5 %. This is no doubt due to the scarcity of experimental results for compositions above 70 % at the time when the older tables were constructed, which necessitated the use of extrapolation.

### Summary.

The partial vapour pressures of nitric acid and water over nitric acid-water mixtures have been determined in a special apparatus over the range of compositions from 50 % to 100 % nitric acid, at 20° and 0°. The values at intermediate temperatures have been calculated from these. The heats of dilution of nitric acid (50-100 %) have been determined and a new value (much higher than the only available one due to Berthelot) has been obtained for the heat of vaporisation of pure nitric acid.

Our thanks are due to Messrs. Imperial Chemical Industries for permission to publish this paper.

*The Nobel Laboratories,  
Ardeer.*

# STUDIES IN ELECTRODE POLARISATION. PART II. THE INVESTIGATION OF THE RATE OF GROWTH OF POLARISATION POTENTIALS.

BY A. HICKLING.

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In recent years considerable interest has centred around the rate at which polarisation potentials are built up, particularly in connection with the problem of hydrogen overvoltage. The usual method of studying these changes has been to carry out polarisation at a constant current and to apply the voltage between the working electrode and a reference electrode, either with or without valve amplification, to some form of string galvanometer, the movement of which is photographed on a film moving at a constant speed. After suitable calibration, measurement of the track produced permits the construction of a graph of the polarisation potential plotted against the quantity of electricity passed.<sup>1</sup> This method, while capable of considerable accuracy, is attended by a number of difficulties which may be briefly summarised :

(a) Only minute polarising currents can be used, since at high speeds the inertia of the mechanical oscillograph becomes appreciable and causes distortion of the track.

(b) Rigorous precautions are necessary to remove all traces of depolarisers from the electrolytic cell, *e.g.* oxygen in studying hydrogen overvoltage, since these may change markedly the shape of the track obtained.<sup>2</sup>

(c) Since a single polarisation process only is studied in each experiment, it is necessary initially to have the electrode in a reproducible virgin state if the result is to have any general significance.

(d) The quantity of electricity passed is not directly recorded, and any fluctuation in the polarising current or the speed of the camera film will lead to an error in computing this quantity.

(e) The method is extremely laborious and time consuming, and requires a considerable quantity of rigidly mounted mechanical apparatus. Moreover, the required graph can only be obtained by measurement and calculation subsequent to each experiment, and direct visual observation of the building up of the polarisation potential is precluded.

The present method was devised to eliminate these difficulties. It utilises a cathode ray oscillograph as indicating instrument,<sup>3</sup> and by a

<sup>1</sup> Bowden and Rideal, *Proc. Roy. Soc. A*, 1928, **120**, 59; Baars, *Sitzungsber. Ges. Beförd. Naturw. Marburg*, 1928, **63**, 213; Brandes, *Z. physikal. Chem.*, 1929, **142**, 97; Erdey-Grúz and Volmer, *ibid.*, 1930, **150**, 203; Erdey-Grúz and Kromrey, *ibid.*, 1931, **157**, 213. For early work on the oscillographic study of polarisation processes, see Le Blanc, *Abhdlg. d. Buns.-Ges.*, 1910, No. 3; Reichinstein, *Z. Elektrochem.*, 1909, **15**, 734, 913; 1910, **16**, 916.

<sup>2</sup> Cf. Bowden and Rideal, *loc. cit.*<sup>1</sup>

<sup>3</sup> Butler and Pearson, *Trans. Faraday Soc.*, 1938, **34**, 1163, made use of a cathode ray oscillograph as indicating instrument for the study of the growth of polarisation potentials at high currents. Their method is fundamentally different from that to be described here, however, and in any general application is still open to most of the disadvantages listed; moreover, it involves the photography of high speed transients.

special electrical circuit, free from moving parts, it is arranged that the polarisation process is repetitive, leading to a stationary image on the oscillograph screen showing directly the variation of polarisation potential with quantity of electricity passed. The presence of small quantities of depolarisers has no effect on the shape or slope of the section of the graph portrayed, but affects only its extent; furthermore, since the pattern obtained is the mean of a number of polarisations, it is largely independent of the initial state of the electrode. Direct visual examination of the effect of variable factors on the polarisation process is possible, and the results may be photographically recorded at leisure.

### Experimental.

In the present method the polarising current is supplied from a high voltage direct current source, transmitted through a saturated diode which serves to maintain it substantially constant, and then passed into a condenser which is connected in series with the electrolytic cell. Connected across the condenser-cell section of the circuit is a thyatron valve, the trip voltage of which can be controlled by varying the grid potential. While the condenser is being charged, a steady current, which can be adjusted to any desired value, flows through the electrolytic cell, but when the condenser voltage reaches that required to trip the thyatron, the arrangement is short circuited and the condenser discharges, a quantity of electricity exactly equal to that originally passed flowing rapidly through the cell in the reverse direction; the process then repeats itself indefinitely. The voltage between the electrode of the cell which is being studied and a suitable reference electrode is amplified by means of a valve amplifier, and applied to the Y-deflecting plates of a cathode ray tube, while the voltage developed across the condenser (which is exactly proportional to the quantity of electricity passed at any time) is applied directly to the X-deflecting plates of the tube. Under these conditions, the track on the oscillograph screen represents directly the variation of potential of the working electrode with the quantity of electricity passed through the cell, and if the process is reproducible the track appears stationary. The occurrence of a stationary image implies that exactly the same change of potential is brought about on charging the electrode as on discharging it, *i.e.* that there is no irreversible loss of electromotively active material from the electrode. If the electrode is polarised and the pulsating current then switched on, the oscillograph track is usually found at first to move downwards, but in a few seconds becomes stationary; thus automatically only the reproducible portion of the polarisation curve is recorded. The presence of a depolariser which reacts irreversibly with the electromotively active material at the electrode, lowers the maximum polarisation potential which is recorded but cannot affect the shape or slope of that section of the polarisation curve which is portrayed, provided, of course, that the depolariser is not present in such large quantities as to prevent entirely the formation of a stationary image.

In this way the method serves to isolate that part of the polarisation curve which is unaffected by loss of electromotively active material and by accidental variation in the state of the electrode, and the results may therefore be presumed to be indicative of the true course of the polarisation process. The quantity of electricity passed at each pulse can be varied by changing the size of the series condenser, and hence any section, large or small, of the polarisation curve can be studied in detail.

The electrical circuit of the apparatus, constructed for the study of cathodic polarisation processes, is shown in Fig. 1. Current was supplied from an 800 V. rectifier, passed through a milliammeter and bright emitter valve  $V_1$ , the latter serving as a saturated diode, the current being adjustable by varying the filament current by means of the rheostat  $R_1$ , and then



amplifier so as to give suitable reference lines at fractions of a volt on the oscillograph screen.

The form of the electrolytic cell is shown in Fig. 2. The anolyte was contained in a tall beaker and in it was immersed the cathode chamber which was stopped at its lower end with a tight filter paper plug to prevent mixing of anolyte and catholyte. The cathode compartment was fitted with a rubber bung carrying the cathode, the siphon connecting the cathode to the calomel electrode, and a glass tap for introduction of gas; a side tube led to a washbottle containing water. The anode was in general a piece of platinum foil, and the cathode was varied as described below.

### Results.

**Hydrogen Overvoltage.**—In order to test the application of the method, the building up of hydrogen overvoltage was studied, since in this case the general nature of the process has been established by earlier workers.

A freshly amalgamated copper cathode, of 1 sq. cm. area, was used with N.-sulphuric acid as electrolyte. The acid solution was boiled out to get rid of dissolved air prior to introduction into the cell, and then steady electrolysis at 0.025 amp. was carried out for ten hours to displace the bulk of air in the cathode chamber and to polarise the electrode. The direct current was then stopped, the pulsating current switched on, and observations of the oscillograph tracks recorded under various conditions. The results are shown in Fig. 3 (Plate V). In Fig. 3A is shown the polarisation graph with a 0.05  $\mu\text{F}$ . condenser in series with the cell and polarising currents of  $10^{-3}$  and  $10^{-4}$  amp./sq. cm. respectively; the reference potentials in this, and in all subsequent cases, are expressed on the hydrogen scale. It is to be noted that the potential varies linearly with the quantity of electricity passed, and is practically independent of current density. To explore a larger section of the polarisation curve, the capacity of the series condenser was increased to 0.1  $\mu\text{F}$ . and the tracks again recorded. The results are shown in Fig. 3B and it is seen that the linearity of the polarisation process is maintained. The quantity of electricity delivered at each pulse can readily be worked out from a knowledge of the capacity of the series condenser and the voltage to which it is charged; this latter quantity is directly determined by comparing the horizontal deflection on the oscillograph with that produced by standard voltages. Hence the capacity of the double layer at the electrode, which is supposed to be involved in the building up of the hydrogen overvoltage, can be evaluated. Measurement of Figs. 3A and 3B give a value of 10.11  $\mu\text{F}$ /sq. cm. Bowden and Rideal<sup>2</sup> obtained a value of 6  $\mu\text{F}$ . for mercury and 7  $\mu\text{F}$ . for freshly amalgamated silver under somewhat different conditions, while indirect measurements of the capacity by various methods give a value of ca. 20  $\mu\text{F}$ . at a mercury surface.<sup>4</sup> It has been suggested<sup>4</sup> that the low values obtained by the direct methods of investigation are due to contamination of the surface studied, and this factor may be operative in the present experiments; it should be noted, however, that the same value was obtained in numerous experiments under a variety of conditions.

As has been previously stated, the shape and slope of the polarisation graph, as determined by the present method, should be independent of the presence of small quantities of air in the apparatus. To test this point, the value of the capacity of the series condenser was reduced to approximately 0.02  $\mu\text{F}$ ., so that a small section only of the graph was explored, and after the electrode had been polarised as above, air was slowly admitted to the cell; the current density was  $10^{-4}$  amp./sq. cm. The track on the oscillograph screen moved slowly downwards, indicating

<sup>4</sup> See Proskurnin and Frumkin, *Trans. Faraday Soc.*, 1935, **31**, 110.

decreasing polarisation, and three successive photographs were taken. These are reproduced in Fig. 3c. It is seen that although the maximum overvoltage obtained is different in each of the three cases, the linearity and slope of the graph is not appreciably affected by the presence of air.

**Polarisation in the Deposition of Nickel.**—Electrodeposition of Fe, Co, and Ni from solutions of their simple salts does not commence until the cathode potential is distinctly more negative than the reversible values.<sup>5</sup> This type of polarisation, which is apparently peculiar to these metals, is most markedly shown by Ni; thus, according to Glasstone,<sup>6</sup> the reversible potential of Ni in a N-sulphate solution is  $-0.23$  V., but on electrolysis at room temperature deposition of metal does not commence until a cathode potential of about  $-0.57$  V. is reached. Foerster and Georgi<sup>7</sup> claim to have observed Ni deposition from a chloride solution at a cathode potential of  $-0.40$  V. at  $18^\circ$ , but it is doubtful whether it takes place much closer to the reversible potential even at very low current densities. Numerous suggestions have been made to account for this type of overvoltage,<sup>8</sup> and they fall generally into two classes: on the one hand, it has been postulated that the metal is deposited in some peculiarly active form which has a more negative potential than that of the metal in the normal stable state, while on the other hand, it has been suggested that the process of ionic discharge is slow and requires a certain energy of activation, *i.e.* a view essentially similar to that now adopted for the neutralisation of hydrogen ions. The present method would seem to afford a means of distinguishing between these two general views. If the overvoltage is due to some active form of Ni, then it is to be expected that in the initial building up of the polarisation the potential will either vary discontinuously with the quantity of electricity passed or else logarithmically if the active substance forms a solid solution in the cathode surface, while if the process of ionic discharge is slow, leading to the charging up of a double layer at the cathode surface, a linear variation of potential with quantity of electricity passed is to be anticipated.

To test this, an electrode of Ni wire of area 1 sq. cm. was used as cathode and solutions of Analar  $\text{NiSO}_4$  in a buffer mixture of 0.5 N-sodium acetate + 0.5N-acetic acid (approx.  $p_H$  4.6) employed as catholyte. The anode was of platinum foil and the anolyte was dilute sulphuric acid. Prior to each observation, the air in the cathode chamber was displaced by a current of hydrogen; steady electrolysis was then carried out for two minutes at the current density to be used subsequently, and finally the pulsating current was switched on and the oscillograph track observed. Some of the results obtained are shown in Fig. 4 (Plate V). In Fig. 4A is shown the polarisation graph using a current density of  $10^{-3}$  amp./sq. cm. with a N- $\text{NiSO}_4$  solution, there being a  $4\mu\text{F}$ . condenser in series with the cell. The track on the oscillograph screen was very steady and showed little sign of decay even on admitting oxygen to the cell. It is to be noted that the graph is accurately linear up to a potential of about  $-0.4$  V., where it begins to round off, the potential then approaching asymptotically a

<sup>5</sup> Schweitzer, *Z. Elektrochem.*, 1909, **15**, 602; Schildbach, *ibid.*, 1910, **16**, 967; Foerster, *Abh. Bunsen-Ges.*, 1909, No. 2; Glasstone, *J.C.S.*, 1926, 2887.

<sup>6</sup> Glasstone, *loc. cit.*<sup>5</sup>

<sup>7</sup> Foerster and Georgi, *Z. physikal. Chem., Bodenstein Festband*, 1931, 543.

<sup>8</sup> See, for example, Le Blanc, *Trans. Faraday Soc.*, 1914, **9**, 251; Foerster, *Z. Elektrochem.*, 1916, **22**, 85; Smits, *Trans. Faraday Soc.*, 1924, **19**, 772; Kohlschütter, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 229; Glasstone, *loc. cit.*<sup>5</sup>; Thon, *Comptes rendus*, 1933, **197**, 1312.

constant value of rather less than  $-0.5$  V. The effect of variation of current density is shown in Fig. 4B, which was obtained with currents of 2, 1 and  $0.5 \times 10^{-3}$  amp. severally, other conditions being as before. The general features of the graphs are the same, but with decreasing current density the slope of the linear portion becomes rather less and the ultimate potential attained is slightly lowered. Decrease of the Ni ion concentration does not affect the general form of the graph, but the slope of the linear portion is increased, as is shown in Fig. 4C, which was obtained with a 0.1N.-NiSO<sub>4</sub> solution and a current density of  $10^{-3}$  amp./sq. cm.

The results indicate quite conclusively that the essential process responsible for overvoltage in the deposition of Ni leads to a linear variation of potential with quantity of electricity passed up to the point at which metal commences to separate, and this is in conformity with the view that the polarisation is due to a slowness of ionic discharge leading to the charging up of a double layer at the cathode. The capacity of this double layer can be readily evaluated from the oscillograms, and is found to be 430-470  $\mu$ F. per sq. cm. for a N.-NiSO<sub>4</sub> solution electrolysed at current densities of  $2 \times 10^{-3}$  to  $0.5 \times 10^{-3}$  amp./sq. cm. The precise physical significance of a double layer of so high a capacity cannot be assessed without accurate data on the accessible area of nickel under the conditions of experiment.

### Summary.

1. A new method of studying the rate of growth of polarisation potentials is described which gives a stationary image on the screen of a cathode ray oscillograph showing directly the variation of potential with quantity of electricity passed.
2. The method has been tested by applying it to the study of the growth of hydrogen overvoltage at a mercury surface, and results in general conformity with those of previous workers have been obtained.
3. The growth of overvoltage in the deposition of nickel has been studied, and it is found that the potential varies linearly with quantity of electricity passed, up to the point at which separation of metal begins. The results support the view that this type of polarisation is due to slowness of the discharge of the metallic ions.

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# SYSTEMATICS OF BAND-SPECTRAL CONSTANTS. PART V.\* INTERRELATION OF DISSOCIATION ENERGY AND EQUILIBRIUM INTERNUCLEAR DISTANCE OF DI-ATOMS IN GROUND STATES.

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## 1. Introduction.

Attempts are made in the present communication to find reliable means of calculating the dissociation energies of di-atoms in ground states. In the present incomplete state of the quantum-mechanical developments, the author has confined himself to empirical methods. The argument is necessarily based upon a limited number of experimental values, which appear, however, to be known with considerable certainty. Knowledge of ground state dissociation energies in conjunction with excitation energies may facilitate the calculation of dissociation energies from excited states. The first part of the paper deals with non-hydrides: in section 5 hydrides are considered.

Dissociation energy  $D$  is expressed in volts, no distinction being made between  $D_e$  and  $D_0$  (from the zero vibrational level).

Expressions for  $D$  previously suggested vary according to the form chosen for the potential energy-nuclear distance function.

Morse,<sup>1</sup> using his exponential function, obtained the relation

$$D = 1.23 \times 10^{-4} \omega_e^2 / (4\omega_e x_e), \quad (1)$$

where  $\omega_e$ ,  $\omega_e x_e$  are in  $\text{cm}^{-1}$ . It appears that the estimates of  $D$  using this expression tend to be too high where comparison with experiment is possible.

Huggins<sup>2</sup> used a modified Morse potential energy function, and obtained a partly empirical relation which may be written

$$D = 7.4 \times 10^{-7} M \omega_e^2 / [(33 + 0.72 M \omega_e x_e)^{\frac{1}{2}} - 7], \quad (2)$$

where  $M = AA'/(A + A')$ ,  $A$  and  $A'$  being the weights of the two atoms concerned ( $O = 16$ ). This relation tends to give lower and generally more accurate values of  $D$  than (1), but it applies only to molecular groups  $n = 8$  to 14 in the KK period, where the average error in  $D$  is 0.7 volt.

Sutherland<sup>3</sup> has more recently used a potential function involving inverse powers of  $r$ , and has deduced a relation which may be written in the form

$$D = 3.68 \times 10^{-6} M \omega_e^2 r_e^2 / p, \quad (3)$$

where  $r_e$  is equilibrium internuclear distance in A, and  $p$  is the product of the attraction and repulsion exponents of  $r$  in the potential function.

\* Parts I, II and III are in these *Transactions*, 1937, 33, 1390, and Part IV, 1938, 34, 1324.

<sup>1</sup> P. M. Morse, *Physic. Rev.*, 1929 (ii), 34, 57.

<sup>2</sup> M. L. Huggins, *J. Chem. Physics*, 1935, 3, 473; 1936, 4, 308.

<sup>3</sup> G. B. B. M. Sutherland, *Proc. Ind. Acad. Sci.*, 1938, 8, 341.

The value of Sutherland's product is approximately the same for di-atoms of similar electron structure in ground states.

The present author, in a preliminary note,<sup>4</sup> has suggested the relation

$$D = k/(r_e^3 n^{\frac{1}{2}}), \quad (4)$$

where  $n$  is the group number of a non-hydride di-atom, and  $k$  is its period or sub-period dissociation constant. This relation also applies only to ground states.

Comparing (4) with the Morse-Clark formula (see Part IV), it appears that proportionality between  $\omega_e$  and  $D$  is involved. If we calculate  $D$  from the relation  $D = \omega_e/313$ , however, an average error of 1.7 per cent. is found for the test cases LiLi, NN and OO, whereas (4) gives only 0.4 per cent. The constant in the Morse-Clark formula is slightly different for LiLi ( $ss$  type) from that for NN and OO ( $pp$  type), so that constancy of  $\omega_e/D$  will not be exact. Moreover, the Morse-Clark constant takes a different value for di-atom ions in a given period. Out of a considerable variety of relations which have been tried, (4) appears to be the best, and it is also in conformity with the previous finding that  $Dr_e^3$  is constant for carbon-carbon linkages.<sup>5, 6</sup>

## 2. Symmetrical (Elementary) Di-atoms of the KK Period.

Table I shows the results of calculation on three elementary di-atoms of the KK period, whose  $D$  values appear to be accurately determined.

TABLE I.

Di-atom.	$n$ .	$M$ .	$r_e$ .	$\omega_e$ .	$\omega_e r_e$ .	$D$ (expt.).	$\omega_e/D$ .	Calculated Values.				
								$D(1)$ .	$D(2)$ .	$p(3)$ .	$k(4)$ .	$D(4)$ .
LiLi .	2	3.5	2.670	351.4	5.18	1.14	308	0.7	—	9.9	30.7	1.14
NN .	10	7	1.094	2359.6	14.44	7.35	321	11.9	8.7	23.4	30.4	7.39
OO .	12	8	1.204	1580.3	11.99	5.09	311	6.4	4.8	20.9	30.8	5.06

$D$  calculated by (1) does not give satisfactory agreement with experiment, whilst  $D(2)$  is closer for NN and OO. Sutherland's  $p$  separates the cases,  $p(\text{LiLi})$  being different, whilst  $p(\text{NN}) > p(\text{OO})$ . The function  $k = Dr_e^3 n^{\frac{1}{2}}$  is sensibly constant, giving mean  $k = 30.6$ , which therefore gives very good values of  $D(4)$ .

Fox and Martin<sup>6</sup> find  $p = 20.7$  for CC links, close to  $p(\text{OO}) = 20.9$ . Table II shows calculated values of  $D$  for FF and CC, assuming  $p(\text{FF}) = 20.7$ .

TABLE II.

Di-atom.	$n$ .	$M$ .	$r_e$ .	$\omega_e$ .	$\omega_e r_e$ .	$k$ .	Calculated Values.		
							$D(1)$ .	$D(3)$ .	$D(4)$ .
CC .	8	6	1.31	1641.6	—	30.6	—	4.9	4.8
FF .	14	9.5	1.33 <sup>7</sup>	1081 <sup>8</sup>	9.9	30.6	3.6	3.5	3.5

<sup>4</sup> C. H. D. Clark, *Nature*, 1939, 144, 285.

<sup>5</sup> *Ibid.*, 143, 800.

<sup>6</sup> J. J. Fox and A. E. Martin, *J. Chem. Soc.*, 1939, 884.

<sup>7</sup> C. H. D. Clark, *Nature*, 1934, 99, 134.

<sup>8</sup> C. H. D. Clark, *Trans. Faraday Soc.*, 1935, 31, 585.

The agreement between  $D(3)$  and  $D(4)$  is satisfactory in the two cases. The mean value  $D(\text{CC}) = 4.85$  is lower than Mulliken's estimate,<sup>9</sup> 5.5, which is uncertain.  $D(\text{FF}) = 3.5$  agrees fairly well with Desai's thermal value,<sup>10</sup>  $3.3 \pm 0.1$ . The higher figure is supported by the value from Morse's equation  $D(1) = 3.6$ . Morse's equation gives a good fit for  $\text{ClCl}$ , but gives errors increasing from  $\text{BrBr}$  to  $\text{II}$ , so it may apply to  $\text{FF}$ .

### 3. Sutherland's Product as a Periodic Function.

The results of the preceding section suggest that Sutherland's product  $p$ , whilst closely alike for di-atoms of similar configuration, varies somewhat for a given configurational type with group number. Amongst the symmetrical di-atoms of  $\text{KK}pp$  type, it would appear that  $p$  reaches a maximum for  $n = 10$ , in common with other spectroscopic functions  $\omega_e$  and  $k_e$  (bond constant).<sup>11</sup> This view appears somewhat strengthened when attention is paid to unsymmetrical  $\text{KK}$  di-atoms and to  $\text{KK}^+$  di-atom ions.

From equations (3) and (4) we have

$$pk = 3.68 \times 10^{-6} M \omega_e^2 r_e^5 n^{\frac{1}{2}}, \quad (5)$$

which, since  $k_e \propto M \omega_e^2$ , is essentially a function of  $k_e$ ,  $r_e$  and  $n$ . Values of  $pk$  are:  $\text{NN}$  711,  $\text{CO}$  692, and  $\text{CN}$  667. If  $p = 20.7$  for  $\text{CO}$  and  $\text{CN}$ ,  $k = 33.4$  and  $32.3$  respectively, values greater than the above  $\text{KK}$  constant 30.6; but if  $p(\text{CO}) = p(\text{NN}) = 23.4$ ,  $k(\text{CO}) = 29.6$ . (The remaining discrepancy may indicate a further variation of  $p$  with sub-group,  $\text{NN}$  being in the 10s and  $\text{CO}$  in the 10b sub-group of the classification,<sup>12</sup> but this possible refinement is not at present taken into account). We shall study the effect of a continuous variation of  $p$  with  $n$  in the  $\text{KK}$  and  $\text{KK}^+$  periods for  $pp$  type di-atoms, taking  $p = 21.5$  in groups 9 and 11 on each side of the maximum, and so obtaining the  $D(3)$  values of Table III. The values of  $D(4)$  are obtained by keeping  $k = 30.6$  for all cases, and calculated values  $D(1)$  and  $D(2)$  are included for comparison.  $D(\text{J})$  and  $D(\text{S})$  refer to estimates quoted by Jevons<sup>13</sup> and Sponer<sup>14</sup> respectively, the values in brackets being generally less reliable.

TABLE III.

Di-atom	BeO	BeF	BO	CO <sup>+</sup>	CN	NN <sup>+</sup>	CO	NO	OO <sup>+</sup>
$n$	8	9	9	9	9	9	10	11	11
Sub-group	c	c	b	b	a	a	b	a	a
$D(1)$	5.8	5.4	9.3	10.0	10.0	9.3	10.9	7.7	6.6
$D(2)$	4.6	4.7	7.2	7.5	7.6	6.9	8.2	5.7	4.8
$D(3)$	4.0	3.1	5.7	7.1	6.5	7.2	6.5	6.1	6.3
$D(4)$	4.6	4.1	5.9	7.4	6.4	7.4	6.7	6.1	6.2
$D(\text{J})$	—	(6.0)	(6.6)	7.1	—	6.8	(10.0)	(6.1)	6.2
$D(\text{S})$	(5.8)	—	—	—	6.7	6.3	(9.6)	5.3	6.4

<sup>9</sup> R. S. Mulliken, *Rev. Mod. Physics*, 1932, 4, 1.

<sup>10</sup> M. S. Desai, *Proc. Roy. Soc., A*, 1932, 136, 76.

<sup>11</sup> C. H. D. Clark, *Proc. Leeds Phil. Soc.*, 1935, 3, 26.

<sup>12</sup> C. H. D. Clark, *Trans. Faraday Soc.*, 1935, 31, 1017.

<sup>13</sup> W. Jevons, *Report on Band-Spectra of Diatomic Molecules (Appendix II.)*, 1932, Camb. Univ. Press.

<sup>14</sup> H. Sponer, *Molekülspektren und ihre Anwendung auf chemische Probleme. I. Tabellen*, 1935, Berlin, Julius Springer.

As previously noticed,  $D(1)$  tends to give rather too high values, and  $D(2)$  is observed to be smaller than  $D(1)$ .  $D(2)$  involves an empirical factor<sup>2</sup> of 0.8, which may not always be suitable, but the results are probably nearer the truth than those of  $D(1)$ . On the other hand, the generally satisfactory agreement between  $D(3)$  and  $D(4)$  previously found for CC and FF in this period is maintained. It is noteworthy that BeO and BeF give poor agreement, but since these di-atoms are of  $sp$  type, it appears that a different value of  $p$  should be used in calculating  $D(3)$ .

Comparing the results with the estimates  $D(J)$  and  $D(S)$  based upon experimental data, the mean of  $D(3)$  and  $D(4)$  agrees satisfactorily for  $CO^+$ ,  $OO^+$  and CN, less well for  $NN^+$  and NO. There is striking divergence in the case of CO, but here the dissociation energy is still uncertain, in spite of extensive discussion of the data.<sup>15</sup> It appears well established that if the dissociation of both CN and CO is into unexcited atoms,  $D(CO)$  should be greater than  $D(CN)$  by about 3.2 volts. All the four methods of calculation used in compiling Table III, however, agree in making the difference much smaller than this. It may be pointed out that a difference of 3.2 is incompatible with even approximate equality of  $p(CN)$  and  $p(CO)$ . The difficulty might be resolved if CN does not dissociate from the ground state into normal atoms.

Table III further suggests that the periodicity of dissociation energies follows a plan similar to that previously found for fundamental vibration frequencies,<sup>11</sup> with maximum values in group X, and decreasing values with increasing sub-group asymmetry: thus  $D(CN) > D(BO) > D(BeF)$  in sub-groups IXa, IXb and IXc respectively. This would suggest  $D(CO) < D(NN)$ , which has not been so far proved by experiment. Apart from some uncertainty, the agreement between calculated and the most reliable experimental estimates may be judged generally satisfactory. The methods adopted afford considerable systemisation of the data on the related di-atoms of the KK and  $KK^+$  periods, and provide evidence of the suggested periodicity of Sutherland's product.

The above considerations appear largely upheld by similar calculation in the KL and LK periods on  $pp$  type di-atoms, where we have the experimental result  $D(SO) = 5.053$ . This with  $r_e = 1.489$  gives  $p(3) = 21.8$ , and  $h(4) = 57.8$ . If we keep  $k$  constant and assume a similar periodic variation of  $p$  with  $n$  to that used in the KK period, we obtain Table IV. We take  $p = 24.3$  for  $n = 10$ ,  $p = 22.4$  for  $n = 9$  and 11, with the above  $p = 21.8$  for  $n = 12$ .

TABLE IV.

Di-atom	AlO	CP	SiN	CS	SiO	PN	PO
Group	9	9	9	10	10	10	11
Sub-group	b	a	a	b	b	s	a
$D(3)$	4.1	5.3	5.0	5.1	5.4	5.8	5.5
$D(4)$	4.6	5.1	5.0	5.1	5.4	5.6	5.8

The agreement between  $D(3)$  and  $D(4)$  is again satisfactory, except in the case of AlO, where perhaps the less symmetrical sub-group 9b requires a lower  $p$  than 9a. Should the experimental  $D(SO)$  be cor-

<sup>15</sup> G. Herzberg, *Chem. Rev.*, 1937, **20**, 145.

rected, this will affect the values of  $D(3)$  and  $D(4)$ , but since ratios only are involved, it would appear that the measure of agreement between them would remain.

The methods of derivation of  $D(3)$  and  $D(4)$  appear quite independent, and the periodicity of  $p$  has not been suggested to cause them to agree, but to conform with the experimental results of Table I. It appears, however, that another relation of the form (5) is involved, connecting bond constant and internuclear distance.<sup>4</sup> Fox and Martin<sup>6</sup> have reached similar conclusions for C—C links, where  $k_e r_e$ <sup>5</sup> is found to be constant. This matter is receiving further consideration.

#### 4. More Complex Non-hydride Di-atoms.

In Table V we have calculated as many values of  $p(3)$  and  $k(4)$  as possible from  $D(\text{expt.})$  for di-atoms which contain no atom of the K period. The value of  $D(\text{SS})$  is either 3.6 or 3.3 according to Olsson,<sup>16, 17</sup> whilst  $r_e = 1.88$ . Other  $D$  values are taken from Sponer.<sup>14</sup>

TABLE V.

Di-atom	NaNa	PP	SS	ClCl	KK	BrBr	ICl	II
Period	LL	LL	LL	LL	MM	MM	NL	NN
Group .	2	10s	12s	14	2	14	14	14
Type .	ss	pp	pp	pp	ss	pp	pp	pp
$r_e$ .	3.07	1.88	1.88	1.983	3.91	2.28	2.315	2.660
$D(\text{expt.})$	0.76	5.008	3.6    3.3	2.468	0.51	1.961	2.143	1.535
$p(3)$ .	13.3	24.6	30.5   33.3	33.2	18.5	40.9	32.0	49.4
$k(4)$ .	31.1	105.3	82.9   76.0	72.0	43.1	86.9	99.4	108.1

Table V indicates that for LL and higher periods  $k$ , like  $p$ , becomes sensitive to configuration type, being different for the ss di-atoms NaNa, KK from that for the pp cases ClCl, BrBr respectively. Amongst the LLpp cases, the  $p(3)$  values support  $D(\text{SS}) = 3.3$  rather than 3.6, and  $p(\text{PP}) = 24.6$  appears erroneous. Further,  $D(\text{SS}) = 3.3$  gives  $p(3) = 33.3$ , which agrees with  $p(3) = 33.2$  for ClCl. Values of  $D(4)$  which agree with  $k = 72$  are **3.4**, **3.1** for PP, SS respectively. Similarly, taking  $k(\text{SeSe}) = k(\text{BrBr}) = 86.9$ ,  $r_e(\text{SeSe}) = 2.15$ ,<sup>17</sup> and  $k(\text{TeTe}) = k(\text{II}) = 108.1$ ,  $r_e(\text{TeTe}) = 2.59$ ,<sup>17</sup> we obtain  $D(4)$  equal to **2.5** and **1.8** for SeSe and TeTe respectively. Again,  $r_e(\text{PP})$  lies near  $r_e(\text{SS})$ , so if we may take  $r_e(\text{AsAs}) = r_e(\text{SeSe}) = 2.15$ , with  $k = 86.9$ , we obtain  $D(4)$  for AsAs as **2.8**. The  $D$  values found here for SeSe and TeTe are about 0.5 volt smaller than earlier uncertain assignments for these cases, whilst the value for AsAs agrees within 0.2 volt with the lower of the two possible values 4.0 and 2.6 found by Almy and Kinzer.<sup>18</sup>

#### 5. Hydride Di-atoms.

It is characteristic of hydride di-atoms XH that the reduced atomic weight  $M = A/(A + 1)$ , where  $A$  is the atomic weight of X, does not

<sup>16</sup> E. Olsson, *Nature*, 1936, **137**, 745.

<sup>17</sup> E. Olsson, *The Band Spectra of Sulphur, Selenium and Tellurium*, 1938, Dissertation, Stockholm.

<sup>18</sup> G. M. Almy and G. D. Kinzer, *Physic. Rev.*, 1935, (ii), **47**, 721.

vary greatly for small changes in  $A$ , and approaches unity as  $A$  increases, whilst the reduced mass  $\mu = 1.65M$  approaches the value 1.65.

If we eliminate  $\omega_e$  between the Morse-Clark formula (see Part IV) and Sutherland's relation (3), we obtain  $pDr_e^4n = 3.68 \times 10^{-6}MK_{gr}^2$ , where  $K_{gr}$  is the sub-period constant of the formula. It then follows that for di-atoms whose values of  $p$  and  $M$  do not differ very greatly

$$D = l/(r_e^4n), \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $l$  is a sub-period constant. This formula may be expected to hold for hydrides, in place of (4) applicable to non-hydrides.

Isotopic di-atoms have  $D$  and  $r_e$  closely alike, so we may expect constancy of  $l$  in such cases, although  $M$  varies. Using Beutler's  $D$  values<sup>19</sup> for HH, HD, and DD, it is found that  $l = 2.7$  fits the three cases, a small increase in  $D$  from HH to DD being accompanied by a small decrease in  $r_e$ . Equation (4) should also be suitable for isotopic forms of non-hydrides.

We next apply (6) to the KH and LH periods, using the  $D$  values selected by Berriman and Clark,<sup>20</sup> based on careful comparison of available spectroscopic and thermal evidence. Some of the numbers may be subject to revision, but serve as a basis for discussion. In Table VI values of  $p(3)$  and  $l(6)$  are given.

TABLE VI.

Di-atom.	Period.	$n$ .	Type.	$D$ .	$\mu$ .	$r_e$ .	$p(3)$ .	$l(6)$ .
LiH	KH	2	$s\sigma$	2.47	1.453	1.593*	6.6	31.8
BeH		3		3.22	1.495	1.340	7.8	31.1
BH		4	$p\sigma$	3.45	1.521	1.226	7.4	31.2
CH		5		4.0	1.533	1.12	8.8	31.5
NH		6	$p\pi$	4.47	1.550	1.041	7.9	31.5
OH		7		5.07	1.563	0.974	8.9	31.9
FH		8		6.36	1.578	0.915	7.9	35.7
NaH		2	$s\sigma$	2.28	1.581	1.88	7.5	57
MgH	LH	3	$p\sigma$	1.40	1.585	1.73	16.9	38
AlH		4		3.12	1.592	1.643	8.7	91
SiH		5	$p\pi$	3.27	1.593	1.53	10.3	90
PH		6		2.74	1.599	1.429	15.1	69
CIH		8		4.40	1.604	1.272	11.8	92

\* Value for LiD.

From LiH to FH,  $D$  and  $r_e$  move in opposite directions, whilst  $p$  appears sensitive to structural change, apparently increasing slightly from  $s\sigma$  to  $p\pi$  types. On the other hand,  $l$  is remarkably constant throughout the whole period, except for FH, where perhaps  $D(\text{FH}) = 6.36$  is too high. The Morse formula (1) gives the following values of  $D$ : LiH 2.60, BeH 3.56, OH 5.26, FH 5.52. These numbers run within 0.3 volt of  $D$  for LiH, BeH and OH. If we take  $D(\text{FH}) = 5.52$ , we have  $l(6) = 30.9$ , which is not far from the mean 31.5 of the KH period. If  $l(\text{FH}) = 31.5$ , we have  $D(6) = 5.62$ , which in turn gives  $p(3) = 8.9$ , in agreement with  $p(\text{OH})$ . A self-consistent scheme is thus obtained.

In the LH period, although  $r_e$  falls continuously from NaH to CIH,  $D$  does not move continuously in the opposite direction as in the KH period. This may suggest that some of the  $D$  values are wrong, which

<sup>19</sup> H. Beutler, *Z. physik. Chem., B*, 1934, **27**, 287.

<sup>20</sup> R. W. Berriman and C. H. D. Clark, *Proc. Leeds Phil. Soc.*, 1938, **3**, 465.

appears borne out by the general irregularity of  $p(3)$ . The run of  $l(6)$  suggests it to be a sub-period function depending on electron configuration. The  $l$  values for AlH, SiH and ClH lie near together, suggesting  $l = 91$  for  $p\sigma$  and  $p\pi$  types in this period, in which case MgH and PH do not fit. If  $l = 91$  for MgH,  $D(6) = 3.4$  and  $p(3) = 7$ , which fits better than 16.9 into the sequence; similarly,  $l = 91$  for PH gives  $D(6) = 3.64$ ,  $p(3) = 11.3$ , which lies near  $p(\text{ClH}) = 11.8$ . From NaH to ClH, as from LiH to FH,  $p$  appears to increase with increasing  $n$ .

Results on the meagre data in higher hydride periods are not recorded in detail, but they tend to confirm the variation of  $l$  with electron type in a given period. Further, in the case of the only pair (AgH and CdH<sup>+</sup>) of a given type ( $\bar{\text{N}}\text{H}\sigma$ ) for which comparison is possible the  $l$  values coincide. In these higher periods, the evidence suggests that  $p$  may be periodic, in such a way that a maximum is reached in each period; thus, for example,  $p$  shows the following corresponding sequences: CuH 9.5, ZnH 21.7, BrH 13.4; AgH 12.2, CdH 32.6, IH 16.4.

The more certain period dissociation constants  $k$  and  $l$  are collected in Table VII, which shows that in the KK and KH periods the numbers are independent of sub-period type.

TABLE VII.

	Values of $Dr_e^3 n^{\frac{1}{2}} = k$ .			Values of $Dr_e^4 n = l$ .				
Period . . .		KK	KL	LL		HH	KH	LH
Sub-period type	$\left\{ \begin{array}{l} ss \\ sp \\ pp \end{array} \right.$	30.6	—	31.1	$\left\{ \begin{array}{l} s\sigma \\ p\sigma \\ p\pi \end{array} \right.$	2.7	31.5	57
		30.6	—	—		—	31.5	91
		30.6	57.8	72.0		—	31.5	91

The views expressed in this communication may be capable of considerable extension as the experimental data are augmented. The work described in the present and preceding part of this series of papers appears to emphasise the importance of group number in interrelating spectroscopic constants.

### Summary.

The applicability of the empirical relation  $k = Dr_e^3 n^{\frac{1}{2}}$ , where  $D$  is dissociation energy,  $r_e$  equilibrium internuclear distance,  $n$  group number, and  $k$  a period (or sub-period) constant, has been tested for non-hydride di-atoms in ground states and compared with formulæ suggested by other authors (Morse, Huggins, Sutherland). Consistent results are obtained by Sutherland's and the author's formulæ, provided that the product occurring in Sutherland's expression has periodic character with group number, attaining maximum values in group X in each period. The results also confirm recent work of Fox and Martin on CC linkages.

The corresponding relation for hydride di-atoms is found to be  $l = Dr_e^4 n$ . Consistent results are obtained by Sutherland's and the author's methods.

The results indicate that  $k$  is sensibly constant in the KK period for elementary di-atoms, and possibly for other cases, and that  $l$  is constant in the KH period, but that in other periods  $k$ ,  $l$  are sensitive to electron configuration type.

Comparison with experimental data gives generally satisfactory results. A method is hereby suggested for the rapid approximation of  $D$  from  $r_e$ , whereby certain unknown dissociation energies are calculated.

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## INFLUENCE OF ACIDITY ON CATALYTIC EXCHANGE OF HYDROGEN AND WATER.

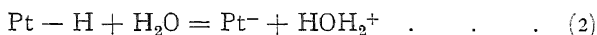
By A. R. BENNETT AND M. POLANYI.

*Received 4th October, 1939.*

The following note is concerned with a factual detail of a complex matter. Immediately following on their first observation<sup>1</sup> of the catalytic interchange of hydrogen and water on platinum black, Horiuti and Polanyi noted<sup>2</sup> that the rate of this reaction was slower in alkali than in acid. Hence they concluded that the rate was not determined by the process



which was at the time thought to be purely homopolar, but that it consists in



which, involving the separation of charges is of a nature to be influenced by potential changes accompanying variations in acidity. The significance of the acidity effect was contested by Butler<sup>3</sup> but maintained by Horiuti and Polanyi.<sup>4</sup> New evidence for the acid-alkali effect was presented by Eley and Polanyi<sup>5</sup> who, having found (similarly to Farkas and Farkas<sup>6</sup>) that there is little if any delay between the splitting up of a hydrogen molecule and its exchange with water, now concluded that it is not (2) but (1) which determined the rates, and that this is influenced by the interface potential in virtue of the polar nature of the Pt — H bond, as evidenced by the work of Slygin and Frumkin.<sup>7</sup> This contention, however, was not accepted by Horiuti and Okamoto<sup>8</sup> who doubted whether poisoning of the metal by impurities of the alkali, as observed in various electrolytes by Volmer and Wick,<sup>9</sup> could not, in conjunction with the activating effects of air, simulate a reversible effect of acidity which does not exist in reality.

Consequently, further experiments have now been undertaken to test the acidity effect using depoisoned alkali and removing the system from contact with air. The results contained in the present paper prove that this change of conditions has no influence: the acidity effect is observed exactly as before. Our experiments were completed when confirmation of the acidity effect also came from Horiuti and Ikusima<sup>10</sup> who, using depoisoned alkali and strong shaking, claim a 100-fold reduction of rate between  $n/10$  HCl and  $n/1$  KOH. Their communication, which seems to be of a preliminary nature, does not

<sup>1</sup> Horiuti and Polanyi, *Nature*, 1933, 132, 819.

<sup>2</sup> *Ibid.*, 931. <sup>3</sup> Butler, *ibid.*, 1934, 133, 26.

<sup>4</sup> Horiuti and Polanyi, *ibid.*, 1933, 132, 931.

<sup>b</sup> Eley and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1388.

<sup>6</sup> A. Farkas and L. Farkas, *ibid.*, 1937, 33, 678.

<sup>7</sup> Slygin and Frumkin, *Acta Physicochimica U.R.S.S.*, 1935.

<sup>8</sup> Horiuti and Okamoto, *Trans. Faraday Soc.*, 1936, 32, 1492.

<sup>9</sup> Volmer and Wick, *Z. physik. Chem.*, 1935, 172, 429.

<sup>10</sup> Horiuti and Ikusima, *Proc. Imp. Acad. Tokyo*, 1939, 15, 39.



mention what tests of reversibility were made and seems to imply that air was not excluded from reaching the catalyst when the liquid was changed; reference is made to further explanations which will be given in a later paper.

### Experimental Method.

#### Materials.

**Catalyst** consisted of platinum foil 0.001 in. thick cut into squares of approximately  $5 \times 5$  mm. and was cleaned by chromic acid and washed with distilled water.

**N. Hydrochloric Acid.**—Woolley's Pure Normal Hydrochloric acid was used.

**N./10 Caustic Potash Solution.**—Prepared by dissolving the requisite weight of Merck's pure KOH in distilled water. This was depoisoned by allowing to stand in contact with platinum black for some weeks.

**Deuterium**, obtained by electrolysis of alkaline  $D_2O$  from Norsk Hydro-Elektrisk Co., was purified by passing it through a heated palladium

thimble. The  $D_2$  concentration was assumed to be 100 %. For experiments in which 60 %  $D_2$ , 40 %  $H_2$  was used the 100 %  $D_2$  was diluted with pure  $H_2$ .

**The Reaction Vessel** before use was cleaned in chromic acid and washed thoroughly with distilled water.

The platinum foil cuttings which were used as the catalyst were placed in the reaction vessel shown in Fig. 1 and immersed to start with either in N./1 HCl or N./10 NaOH. The vessel (connected by a glass spiral with the vacuum apparatus) was filled with deuterium and shaken in horizontal direc-

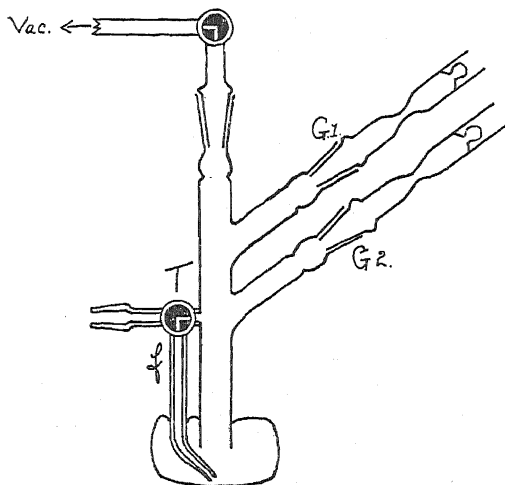


FIG. 1.

tion at an amplitude of about  $\frac{3}{8}$  in., making 4-6 full turns per second. At the end of a run the liquid was removed under hydrogen through the capillary *f* and the two-way tap *T*; a new liquid which had been previously outgassed being then introduced through one of the breakable joints *G1* or *G2*. The liquid was changed a second time under hydrogen through the joint not used in the first instance. This complete cycle was carried out twice; but experiments were also registered in which only one change could be made under hydrogen, because subsequently air came in by leakage or mistake. Such experiments showed that the presence of air has no appreciable effect on the phenomenon.

The deuterium used was 100 per cent. to start with, except in the experiments where the observation of the reaction  $H_2 + D_2 = 2HD$  was intended, in which case an initial concentration of 60 %  $D$  was taken. Changes in concentration were observed by measuring the heat conductivity of the gas. For the  $H_2 + D_2$  reaction the conductivity was read twice: before and after equilibration on a hot wire.

## Results.

In Table I one run is reproduced to show the details of the experimental conditions and the extent to which the exchange velocity constants  $k_e$ , calculated on the basis of a first order reaction, were reproducible. Table

TABLE I.

90 cm.<sup>2</sup> Platinum Foil. 10 c.c. N. HCl.  
Initial Gas. 100 % D. Hydrogen Pressure 103-113 mm.

Date.	Temperature (°C.).	Time (t) (hr.).	% D at Time t.	$k_e$ (hr. <sup>-1</sup> ).
24 I 39	19.4	3.31	46.6	0.230
25 I 39	18.1	4.29	37.7	0.227
25 I 39	18.5	3.17	48.2	0.230
26 I 39	18.0	3.37	44.8	0.240
27 I 39	0.0	5.03	46.0	0.155
27 I 39	0.0	3.93	52.4	0.165
28 I 39	0.0	2.67	66.0	0.156
30 I 39	0.0	3.67	54.4	0.166
30 I 39	19.0	2.10	62.0	0.229
30 I 39	17.2	2.10	59.8	0.246

II surveys the final results of a number of runs. It shows that the substitution of N./10 NaOH for N./1 HCl reduces the rate of exchange by a factor 4-12 at 0° and to a lesser extent at room temperature. This is accompanied by a marked increase in the temperature coefficient, resulting

TABLE II.\*

a and b 90 cm.<sup>2</sup> Platinum Foil (Experiments 12 to 57).  
c and d 150 cm.<sup>2</sup> Platinum Foil (Experiments 72 to 144).  
Hydrogen Pressure 100-127 mm.

Solution.	$k_e$ (0° C.), hr. <sup>-1</sup> .	$k_e$ (20° C.), hr. <sup>-1</sup> .	Log <sub>10</sub> B.	E k.cal./mol.
a { N./10 KOH . . .	0.040	0.134	6.3	9.8
N. . HCl . . .	0.119	0.182	1.8	3.4
b { N. . HCl . . .	0.159	0.240	1.6	3.0
N./10 KOH . . .	0.013	0.037	4.7	8.4
c { N./10 KOH . . .	0.065	0.179	5.6	8.4
N. . HCl . . .	0.269	0.396	1.8	3.0
d { N./10 KOH . . .	0.056	0.146	4.8	7.7
N. . HCl . . .	0.357	0.525	2.0	3.2
N./10 KOH . . .	0.072	0.181	4.1	6.7
N. . HCl . . .	0.271	0.449	2.6	4.1

\* The value of  $k_e$  at 0° C. and 20° C., of B the temperature independent factor, and E the activation energy, were obtained graphically from the experimental values of  $k_e$  at various temperatures. The acid-alkali changes within the groups a, b, c and d were all effected in an atmosphere of H<sub>2</sub>.

in an increase of the calculated activation energy on the average from 3.5 k.cal. in acid to 8.0 k.cal. in alkali. We cannot definitely conclude from our experiments as to what extent the rate of exchange was lowered by the physical factors limiting the rate of diffusion. This would reduce

the apparent effect of changes in acidity while at the same time diminishing the apparent activation energy of the faster reaction. Horiuti and Ikusima<sup>10</sup> have published a single series of observations from which by slight extrapolation a 22-fold reduction of rate in the range of  $N_2/HCl$  to  $N_2/10\ KOH$  is apparent. This may perhaps indicate that even our ratio 12 is still somewhat reduced by the physical factors; but a more detailed consideration of our data, which need not be communicated here, does not make this appear likely.

In Table III some experiments are listed in which the first order

TABLE III.\*

Experiments 12 to 15 and 22 to 25.  
90 cm.<sup>2</sup> of Platinum Foil.

Hydrogen Pressure 100 to 127 mm.  
Initial gas 62.0 %  $D_2$ , 38.0 %  $H_2$ .

Date.	Solution.	Temperature °C.	Time $t$ (hr.).	% $D_2$ time $t$ .	$w_1/w_2$ .	$k_g$ (hr. <sup>-1</sup> ).	$k_c$ (hr. <sup>-1</sup> ).
15 12 38	$N_2/10\ KOH$	21.3	3.23	36.8	0.84	0.162	0.055
16 12 38	"	21.3	5.08	33.4	0.71	0.122	0.066
16 12 38	"	21.0	4.71	34.8	0.76	0.118	0.059
17 12 38	"	19.2	4.50	38.0	0.76	0.108	0.062
5 1 39	$N_2\ HCl$	14.6	5.21	31.0	0.76	0.134	0.053
5 1 39	"	15.4	4.48	30.0	0.79	0.162	0.053
6 1 39	"	16.0	4.17	30.5	0.82	0.171	0.047
6 1 39	"	16.9	5.20	27.0	0.83	0.150	0.036

\*  $k_g = 1/t \log w_2/w_1$  where  $w_1$  is the resistance shift on equilibration of the final gas— $w_2$  is the resistance shift on equilibrating a gas of the same total D atom concentration with no HD present.

"conversion constant"  $k_c$  referring to the  $H_2 + D_2 = 2HD$  reaction was also observed. The resistance shifts from which these are derived are of the order of 0.2 ohms only and the accuracy is correspondingly reduced. Nevertheless, the results leave no doubt that in our experiments the exchange was accompanied by a certain amount of conversion, its rate being  $\frac{1}{3}$  to  $\frac{1}{2}$  of the rate of exchange.

### Discussion.

The communication of these experimental results seems no sufficient occasion to develop all the wider problems of which they form part. But a few remarks may be permitted concerning the new suggestion of Horiuti and Ikusima that the electrode processes on platinum proceed by the "electrochemical mechanism" of Horiuti and Okamoto. This mechanism would appear to be excluded for cathodically polarised electrodes of the metal palladium which is closely similar to platinum. Experiments quoted in this connection by Frumkin,<sup>11</sup> show that the overvoltage spreads by diffusion from one side of a thin palladium foil to the other: this effect proves that the evolution of hydrogen is not, or not principally, due to a lowering of an energy barrier caused by polarisation as in the electrochemical mechanism; but to an accumulation of hydrogen in the valley immediately preceding the significant energy barrier, and that hydrogen in the state corresponding to this valley is diffusible through palladium. To this may be added the experiments of Calvin and Dyas<sup>12</sup> showing that on platinum cathodically

<sup>11</sup> Frumkin, *Acta Physicochimica U.R.S.S.*, 1937, 7, 475.

<sup>12</sup> Calvin and Dyas, *Trans. Faraday Soc.*, 1937, 33, 1492.

polarised to not more than 0.01 volt, the rate of exchange is reduced to a fraction of the rate of  $H_2 + D_2$  conversion—although according to the electrochemical mechanism such conversion should be negligible.

The conversion which we observed ourselves shows that even on unpolarised blank platinum a process of dissociation  $H_2 = 2H$  preliminary to the formation of  $H^+$ -ions does take part in determining the rate of reaction.

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## THE SIMPLEST ULTRACENTRIFUGE WITH PHOTOGRAPHIC RECORDING.<sup>1</sup>

BY JAMES W. MCBAIN AND ALLEN H. LEWIS.

*Received 13th October, 1939.*

The directly air-driven transparent ultracentrifuges<sup>2</sup> require a highly skilled mechanician for their construction. Consequently the cost is more than that of the opaque analytical ultracentrifuges,<sup>3</sup> although still much less than that of the air-driven vacuum type of Beams and others. Furthermore, all of these transparent ultracentrifuges require expensive optical accessories. We have therefore simplified the directly air-driven rotor and dispensed with a camera, producing an ultracentrifuge with which useful results of fair accuracy can be attained in any laboratory with the necessary supply of air.

Briefly, the rotor is a solid piece of duralumin with a cover, holding slit non-conducting blocks each containing a capillary tube for the solution and resting upon a piece of ordinary photographic film. A run is made in dim light or under cover until the record is desired, whereupon the light is flashed on for one or more seconds. The record is thus obtained without stopping the rotor. The normal speed is 72,000 r.p.m., producing a force of 116,000 times gravity at the centre of the cell. A smaller rotor can produce any desired greater force. The present rotor may also be run as slowly as desired to measure sedimentation equilibrium. In this respect it is especially valuable for the study of virus.

### Design of the Rotor.

The design of the rotor is illustrated in Figs 1 (Plate VI), 2, and 3. The rotor consists of a solid piece of duralumin, 7 cm. in diameter, with angle of cone  $102^\circ$ . The top surface is flat, except for a rim 4 mm. wide and 1 mm. high at the periphery. Two or more wells with perpendicular walls are milled into the rotor, each the same distance from the centre of rotation. These wells are 11.5 mm. wide, 10.5 mm. deep and 23 mm. long, with

<sup>1</sup> McBain and Lewis, *Science*, 1939, 89, 611.

<sup>2</sup> McBain and O Sullivan, *J. Amer. Chem. Soc.*, 1935, 57, 780, 2631; McBain and Lewis, presented at *Colloid Symposium*, 1939.

<sup>3</sup> McBain and Alvarez-Tostado, *Nature*, 1937, 139, 1066; *J. Amer. Chem. Soc.*, 1937, 59, 2489; McBain and Leyda, *Nature*, 1938, 141, 913; *J. Amer. Chem. Soc.*, 1938, 60, 2998; McBain, *J. Physic. Chem.*, 1938, 42, 1063; *Chem. Rev.*, 1939, 24, 289.

rounded ends. The cover is made of a single piece of duralumin, and is held to the rotor by a central screw. It has a maximum thickness of 3 mm. near the centre and tapers to be flush with the rim at the edge of the rotor. The under surface of the cover lies flush with the top surface of the rotor. The top surface of the cover is turned as shown in profile in Fig. 2, so that a ring uniformly 2 mm. in thickness is obtained just over the wells in the rotor. In this a slightly tapered hole 9 mm. in diameter, drilled from underneath, takes a glass or quartz window held by Duco cement. The threads of the central screw are ground until when the cover is tight the window is directly over the capillary tube. The cover also contains two small wrench holes for tightening the cover.

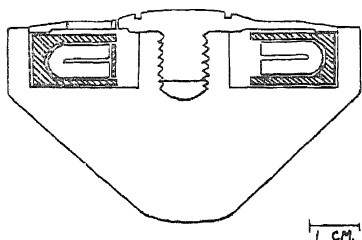


FIG. 2.—Cross-section through assembled rotor.

Two blocks of hard rubber were made to fit snugly into the wells. These blocks are half round at one end and cut off square at the other end. Into each is drilled a horizontal hole 7 mm. in diameter with a rounded bottom, leaving a wall of 3 mm. of hard rubber at the rounded end of the block. These holes are made so that thick-walled capillary tubes of 7 mm. external diameter fit snugly into them. The block which is to hold the tube in which measurement is to be made is sawn nearly in two lengthwise by a vertical cut to let a beam of light pass through. This produces two slits 0.6 mm. wide which are directly opposite each other, one in the centre of the top wall and the other in the centre of the bottom wall. If a small piece of photographic film is placed under the hard rubber block, the light beam places upon the film a shadow reproduction of the capillary tube and its contents. A tiny hole 0.5 mm. in diameter is drilled

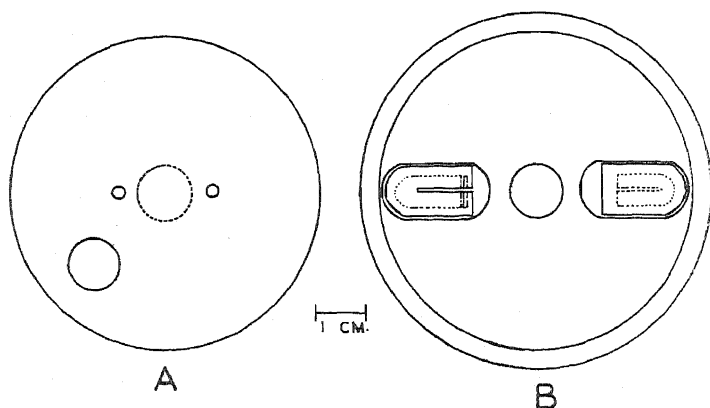


FIG. 3.—View from above, A, cover, and B, rotor containing cell and dummy.

through the cover just next to the window on the side toward the centre of the rotor. Part of the vertical beam of light passes through this hole and places a spot upon the film which is a known distance from the centre of rotation and is used as a reference point for measurement.

The capillary tubes are of glass or quartz of outside diameter about 7 mm. and inside diameter 1 mm. They are sealed at one end, and the open end is ground flat. They are filled with a capillary pipette and then, to prevent evaporation, sealed with a small piece of gummed label and Duco cement. The tubes are about 12 mm. long, thus being about 2 mm.

shorter than the hole in the rubber block into which they fit. A small piece of cork 1 mm. thick is placed over the flat end of the tube after it is placed in the rubber holder, to insulate it from any temperature changes.

A simple 7 cm. stator without central air inlet was used, with 15 air holes of 0.033 in. diameter.

### Operation Characteristics of Rotors.

The relation between speed and the size and number of air ports was investigated by F. A. Leyda and Joseph Grebmeier, using a 5.8 cm. stator (Table I).

TABLE I.

Pressure (lbs./in. <sup>2</sup> ).	Rotor Speed in Revolutions/Second.		
	12 Holes 0.028 in. diam.	24 Holes 0.028 in. diam.	12 Holes 0.033 in. diam.
50	675	780	840
75	725	855	980
100	770	920	1060
125	—	—	1120
150	840	1005	1165
200	860	1060	1180
225	885	—	1200
275	—	1115	—

Raising the number of flutes on the driving cone from 60 to 120 resulted in only a slight increase in speed. Nearly doubling the length of the flutes on the test rotor had practically no effect on the speed.

When the ratio of the number of flutes to the number of air ports is small, it must be an integer, such as  $60/15 = 4$ , if smooth running is to be obtained. When the ratio is large, such as  $120/16$ , it does not seem to matter.

Changing the angle of the rotor cone from  $100^\circ$  to  $110^\circ$  resulted in a marked increase in speed (Table II), and in the Bernoulli effect, but the rotor was not as stable. The instability was due to the greater Bernoulli effect and could be eliminated by use of a stator with adjustable central air inlet.

TABLE II.—EFFECT OF ANGLE OF CONE USING A  $90^\circ$  STATOR.

Pressure (lbs./in. <sup>2</sup> ).	Speed in Revolutions/Second.		
	$100^\circ$ Cone.	$102^\circ$ Cone.	$110^\circ$ Cone.
50	840	870	980
75	980	1030	1160
100	1060	1150	1290

with the vertical baffles. The strips of metal simply rested against the stator at one end and against the top of the guard at the other.

### Use of Capillary Tubes.

Sectorial cells<sup>2</sup> may equally well be employed and made longer and thicker than those for the 37 mm. rotors, but they are much more complicated than ordinary capillary tubes. Objection might be made to these because they are cylindrical rather than radial and sectorial. However, they do in fact give almost perfect results. This must be due to streaming being confined to a few particle diameters on the outside of the

to eliminate vibration visible in the microscope, caused by turbulence of the air, six vertical baffles were attached to the aluminum ring of the stator, each approaching to 1 mm. from the edge of the rotor. In addition, six slanting pieces of metal were placed around the stator, alternating

liquid, producing a very slow controlled and limited movement displacing upwards from the bottom an equal bulk of the total liquid. Thus not only are good boundaries formed and maintained, as observed by Elford, McIntosh and Selbie, and Ford, as well as ourselves, but they move at very nearly the exact theoretical rate.

### Experimental Procedure.

The capillary tube was filled by means of a capillary pipette to about 1 mm. from the top, giving a column of solution about 8 mm. long. Zero time was taken when the air pressure to be used was reached, since the rotor accelerates to speed in a fraction of a minute. The speed of the rotor was measured in the dark by matching the note from an oscillator with that heard directly from the rotor. The temperature was likewise measured. After the run, the rotor was stopped in the dark, wrapped in black cloth and taken to the darkroom, where the film was developed.

Instead of making only one exposure, a movable slit can be used of sectorial shape with limited radius allowing only part of the tube to be photographed at each successive exposure.

### Experimental Results.

**Erythrocrucorin of Earthworm Blood.**<sup>1</sup>—With sharp boundaries such as those for so heavy a molecule ( $s_{20} \times 10^{13}$  observed 59.6, Upsala value 60.9), measurement of the film (Fig. 4, A, B, Plate VI) can be made directly or with a travelling microscope with almost as great accuracy as with the microphotometer.

**Carboxyhemoglobin.**—On the other hand, with the smaller proteins, and only 116,000 times gravity, the boundaries are necessarily diffuse, in accordance with theory. Hence one must distinguish between the point of half-blackening of the film and that of half-concentration, the latter being a close approximation for the ideal for a sharp boundary. The effects were studied as follows.

Horse red blood cells saturated with carbon monoxide were centrifuged with 1 % NaCl five times at 0°, before adding distilled water to rupture the cells and centrifuging off the debris. After dialysis at 0°, some of the crystalline hemoglobin obtained was dissolved in 1 % KCl to study. Exposure was one second with blue light and the films were microphotometered. The point of half-blackening in the first four runs gave distinctly high values 4.8 to 5.6, mean  $5.2 \times 10^{-13}$ , before the illumination was improved by placing a sectorial opening in the optical path to secure uniform illumination. The degree of blackening corresponding to half-concentration is simply determined by photographing in the same tube a solution of half concentration, the two films being developed together (Fig. 4c, d). It was found that the film had to be cut very carefully without exposure, either with a die, or most simply by cutting round an opaque form.

After adopting this technique the values for half-blackening were 6.10 and 6.21, but for half-concentration the results then obtained by L. H. Perry were 4.71 and 4.73 for  $s_{20} \times 10^{13}$  as compared with Steinhardt's Upsala value 4.63.

### Summary.

Details of the construction and operation of the simplest air-driven ultracentrifuge are given, and it is shown that the results are practically as good as those hitherto attained with any of the standard ultracentrifuges.

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## NUCLEAR GOLD SOLS. II. MECHANISM OF FORMATION.

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It is well known that the size of the particles in gold sols prepared by chemical means depends partly on the reducing agents used in their preparation. Hydrazine and hydroxylamine, for example, give large particles of over 50 m $\mu$  radius in the absence of nuclei, whereas alkali thiocyanate or a solution of phosphorus in ether gives very small particles in the size range 1-6 m $\mu$ , sols of this kind being known as "nuclear." There are numerous experimental data relating to the conditions under which the different kinds of sols are produced and to their physical and chemical properties, but two questions of special interest remain unanswered; one relates to the cause of the dependence of particle size on the nature of the reducing agent, the other to the existence of a lower size limit. The present paper is concerned with the first of these problems.

The formation of a gold sol by chemical reduction involves crystallisation from a solution supersaturated with respect to gold, and therefore in experiments in which only the reducing agent is varied we should expect the relative size of the crystals to be determined by the relative speed of the reactions—the slower reaction giving fewer and larger crystals. This simple and obvious inference apparently contradicts what is observed when, for example, a dilute solution of a gold salt is treated on the one hand with hydroxylamine hydrochloride, and on the other with an ethereal solution of phosphorus; in the first case we get a coarse blue suspension by a reaction which is nearly instantaneous, and in the second a red nuclear sol by a reaction which at the ordinary temperature needs about a day for completion. It seems likely that this apparently anomalous behaviour is due to the occurrence, in the second case, of consecutive reactions differing greatly in velocity; we must therefore start by looking for evidence that reactions leading to the production of nuclear sols do in fact occur in at least two stages.

### Faraday Sols.

When a solution of phosphorus in ether is added to a dilute and slightly alkaline solution of a gold compound (usually chloroauric acid), the liquid at once assumes a brown colour which, in about a day at room temperature, more rapidly if heated, changes to the normal colour of a Faraday sol. This colour change suggests the formation of some intermediate product, though it does not prove it, for the brown liquid may contain gold particles which afterwards undergo some structural change associated with change of colour. This question has been discussed<sup>1</sup> but not investigated. Attempts to find the composition of a coagulum from the brown liquid were inconclusive, because although

<sup>1</sup> Galecki, *Koll. Z.*, 1912, 11, 105; Zsigmondy and Thiessen, *Das kolloide Gold*, Leipzig, 1925, 120.



the coagula, after washing with ether, contained phosphorus, it is possible that some or all of it was derived from phosphorus precipitated along with the gold. The only way of removing this uncertainty is to use a method which does not involve the formation of colloidal phosphorus, a condition which would be satisfied by substituting for phosphorus in ether an aqueous solution of phosphine.

The action of phosphine on gold compounds was first described by Mrs. Fulhame<sup>2</sup> in 1794 as follows:—

“A piece of silk, which was immersed in a solution of nitro-muriate of gold in distilled water, and suspended in the air twelve hours to dry, was divided into three parts. One of these was exposed to a stream of phosphorated hydrogen gas; the silk became brown . . . but no reduction took place. Another of these parts was wetted with alcohol, and exposed to the gas; but no sign of reduction could be perceived. The remaining part was wetted with water, and was no sooner exposed to the gas than the reduction commenced over the whole silk, which was soon covered with a bright coat of reduced gold.”

In 1811 Oberkampff<sup>3</sup> obtained from aqueous chloroauric acid a black precipitate which he regarded as gold phosphide, but which Rose<sup>4</sup> considered was metallic gold. The only other relevant observations were made in 1885 by Cavazzi,<sup>5</sup> who found that phosphine precipitated from solutions of gold chloride in alcohol or ether a black gold phosphide ( $\text{AuP}$ ) which was decomposed by air, or by boiling with water or alkalis, forming metallic gold. He also stated that in aqueous solutions gold was obtained, owing to the action of cold water on the phosphide initially formed. The published information thus leaves little doubt that phosphine reduces gold compounds in aqueous solution to the metal, and suggests that the latter may be derived from a previously formed gold phosphide.

### Experimental.

Phosphine was prepared (1) by boiling phosphorus with aqueous potassium hydroxide, and washing successively with concentrated hydrochloric acid and with water, and (2) by the action of water on phosphonium iodide and washing with water; in each case the washed gas was passed over soda-lime, filtered through glass wool, and absorbed in water in a Pyrex flask. In the experiments to be described the results obtained were the same irrespective of the method of preparation of the phosphine.

(a) Addition of 50 c.c. of phosphine solution to 60 c.c. of a solution containing 15 mg. of gold as  $\text{KAuCl}_4$  and  $2.5 \times 10^{-4}$  equivalent of sodium carbonate caused the instant formation of a red sol.

(b) When the above solutions were mixed in the reverse order a yellow sol was first formed, and this changed to reddish-brown in a few seconds; the yellow colour was not regained on dilution. When the amount of gold was reduced to 10 mg. the duration of the yellow colour was increased to about 5 minutes.

(c) A more stable yellow sol (A) was made by adding a solution containing 8.5 mg. Au with a proportionate amount of alkali to a freshly prepared phosphine solution, the resulting sol containing 0.063 mg. Au per c.c. 20 c.c. of A, kept for 2 days in a stoppered flask containing air, changed into a red gold sol; 20 c.c. kept for the same time in a similar flask under nitrogen remained yellow.

<sup>2</sup> Fulhame, *Essay on Combustion*, London, 1794, 63, 114.

<sup>3</sup> Oberkampff, *Ann. Chim. Phys.*, 1811, 80, 140.

<sup>4</sup> Rose, *Pogg. Ann.*, 1828, 14, 184.

<sup>5</sup> Cavazzi; *Gazzetta*, 1885, 15, 40.

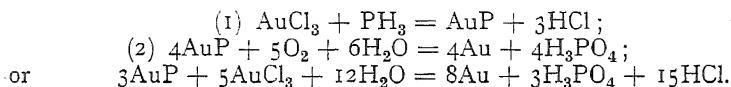
(d) When heated, sol A remained yellow until the boiling point was reached, and then quickly turned red.

(e) A mixture of sol A with a solution of  $\text{KAuCl}_4$  turned red, whilst the same quantity of A exposed to air for the same time remained yellow.

(f) The dispersed material in sol A was analysed after coagulating with sodium chloride and washing the precipitate with water and finally with alcohol. The sol was prepared and coagulated and the precipitate dried in an atmosphere of nitrogen. After weighing, the precipitate was oxidised with nitric acid, and phosphorus was determined by the lead molybdate method,<sup>6</sup> in which the weight of the final product ( $\text{PbMoO}_4$ ) is 1.42 times that of the phosphorus. Two analyses gave P 13.9 and 12.9 %; calc. for  $\text{AuP}$  13.6 %. It is therefore probable that the gold in the yellow sol is present entirely as colloidal auric phosphide.

(g) A further analysis of the coagulum from a sol, originally yellow, which had been allowed to stand over a week-end in contact with air and had turned red, gave P 0.7 %. This coagulum was of the usual bluish-black colour of gold precipitated from a normal gold sol, whereas coagula from the yellow sols were brown. The black precipitates obtained by Oberkamp and by Cavazzi may have owed their colour to admixed gold; in our own experiments the colour of the phosphide precipitates was always brown when adequate precautions had been taken to prevent oxidation.

The experiments just described make it reasonably clear that the primary reaction between phosphine and an auric compound in aqueous solution gives auric phosphide, and that this may be converted into gold under conditions permitting oxidation, *e.g.* by the action of air, boiling water, or excess of gold salt. The reactions may be formulated thus:



According to Cavazzi, in the reaction with water, phosphine and hydrogen are formed in addition to phosphoric acid.

Gold sols made by the phosphine method are nuclear, and can in fact be obtained more finely disperse than any hitherto described. Chemically the reaction is of the kind expected, in that gold is formed only in the last of a sequence of (in this case two) reactions. The Faraday method, in the form described by Zsigmondy<sup>7</sup> is, however, the standard method of preparing nuclear sols, and it still remains to show what relations exist between Faraday sols and those made with phosphine. The first question that arises is whether auric phosphide is an intermediate product in the preparation of Faraday sols. Direct evidence on this matter is not to be had, since the presence of even a large proportion of phosphorus in the coagulum from a sol immediately after mixing the reactants is capable of more than one interpretation. A further difficulty is presented by the fact that auric phosphide sols prepared with phosphine are considerably more stable than are the sols made with a solution of phosphorus in ether; the former are more slowly affected by air, and can be preserved under nitrogen unchanged for more than two months. The experiments described below give further information on these points.

(h) Auric phosphide sol was prepared and afterwards boiled in complete absence of air. The sol turned red within 15 minutes. A similar sol kept at 90° for 7 hours showed no change beyond a slight darkening of colour to yellowish-brown.

<sup>6</sup> Raper, *Biochem. J.*, 1914, 8, 649.

<sup>7</sup> Zsigmondy and Thiessen, *op. cit.*, 48

(i) 1 c.c. of a saturated solution of phosphorus in dry ether was added to 20 c.c. of an ether solution containing 1 mg. of Au as  $\text{HAuCl}_4$ . A yellow sol showing a marked Tyndall effect was formed. Half of this sol was shaken with an equal volume of water: the ether layer was decolorised and the aqueous layer became red. The other half of the yellow sol, when concentrated to one-third of its original volume, deposited a flocculent brown substance having the properties of auric phosphide.

(j) An ethersol of auric phosphide was prepared as in (i). Half of it was shaken with water and gave a red aqueous layer. The other half was shaken with an aqueous solution of phosphine: this gave a yellow aqueous layer. The ether layer was decolorised in both.

The results of these experiments, together with the facts previously established, enable a clear picture to be formed of the succession of events in the formation of nuclear sols whether made with phosphine or with ethereal phosphorus. Thus, when a dilute and slightly alkaline solution of a gold compound is mixed with excess of phosphine a yellow sol of auric phosphide is formed; a yellow hydrosol similar in all respects to the first is also formed by shaking with water the yellow ethersol produced by mixing ether solutions of phosphorus and chloroauric acid; finally, when either of these yellow hydrosols is subjected to the conditions normally prevailing during the preparation of a Faraday sol it is converted into a nuclear gold sol. There is, therefore, a strong probability that auric phosphide is formed as an intermediate product in the Faraday reaction, whilst failure to isolate it from the reaction mixture is adequately accounted for by the fact (*cf.* Experiment j) that oxidation of auric phosphide, though inhibited by phosphine, is not inhibited by phosphorus, and must, therefore, be proceeding at a very early stage, an inference supported by the rapid darkening of the mixture usually observed. The order of mixing (*i.e.* phosphorus is added to the gold compound) would also favour oxidation of the phosphide by the local excess of gold salt during mixing.

Faraday sols have been discussed at some length because of their historical interest and practical importance. The chemical mechanism suggested for their formation is at least highly probable; but the physical mechanism is obscure, owing to our ignorance of whether the initial reaction takes place in solution or is restricted to the surface of the phosphorus particles. This uncertainty, and the difficulty created by the presence of colloidal phosphorus, makes Faraday sols unsuited to further investigation. Sols made with phosphine are free from both these objections, but even they cannot be used in experiments designed to ascertain whether a definite physical connection exists between the particles of the supposed intermediate product and the gold particles finally produced. This question would be resolved if the number of gold particles in the final sol could be shown to be the same as that of the phosphide particles, and this could be done only if the amicroscopic particles were grown to a size large enough to enable them to be counted. The phosphide sols, however, are unstable in the absence of free phosphine, the presence of even a small trace of which would lead to the formation of fresh nuclei and thus nullify any attempt to count the particles.

#### Nuclear Sols made with Hydrogen Sulphide.

When a dilute solution of potassium chloroaurate is mixed with one of hydrogen sulphide in excess, a sol of gold (mainly auric) sulphide is formed; it is at first often turbid owing to the presence of some free

sulphur, but gives a clear yellow sol when boiled. The degree of dispersion of these sols increases with dilution, and when sufficiently dilute they are nuclear, *i.e.* they show only a very weak Tyndall effect, and give rise to nuclear gold sols. The conversion of a sulphide sol into a gold sol can be effected, as with the phosphide sols, by oxidation; but unlike the latter, sulphide sols are stable towards air and are unaffected by boiling, even when free from hydrogen sulphide. They can, therefore, be used for finding what relation exists between the number of sulphide particles and the number of particles in gold sols formed from them.

Auric sulphide sols can be converted into gold sols by treatment with potassium chloraurate, ammonium persulphate, hydrogen peroxide, or ozone; in these reactions the concentrations must be kept low, since all the sulphur appears as sulphuric acid, the coagulating effect of which is added to that of the electrolyte already present and of any which may be derived from the oxidising agent used. The following are examples of the preparation and properties of the sols. The initial sulphide sol was in every case freed from hydrogen sulphide by boiling and by subsequently bubbling filtered air through the liquid for 30 minutes.

**Reaction with Chloraurate.**—3 mg. of Au as  $\text{KAuCl}_4$  were added to 50 c.c. of a  $\text{Au}_2\text{S}_3$  sol containing 1 mg. Au and  $3.5 \times 10^{-4}$  equivalent  $\text{Na}_2\text{CO}_3$ . After 15 minutes the solution became pink, and the colour increased in depth for several days, gradually acquiring a smoky shade. After 8 days slight surface coagulation was visible, and after 1 month the gold was almost completely coagulated. More dilute sols were red, not smoky, but even these coagulated spontaneously in a few weeks. If alkali was omitted the sequence of changes was the same, but coagulation set in earlier. Dilute red sols formed by this reaction are amicronic, but owing to their instability are useless for the purpose in view.

**Reaction with Ammonium Persulphate.**—20 c.c. of a  $\text{Au}_2\text{S}_3$  sol to which was added 1 mg. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  showed no change on standing overnight at room temperature. The sol was then boiled; it turned pink, with a brown tinge, in 10 minutes. The colour was not changed by further boiling. The sol showed only a very faint Tyndall effect.

**Reaction with Hydrogen Peroxide.**—1 c.c. of 6 %  $\text{H}_2\text{O}_2$  (Merck's Perhydrol diluted) was added to 25 c.c. of  $\text{Au}_2\text{S}_3$  sol containing 0.1 mg. Au. No immediate reaction occurred in the cold, but on boiling the liquid became red in 10 minutes. When  $\text{Na}_2\text{CO}_3$  was added in amount sufficient to neutralise the acid formed oxidation occurred slightly less readily. The reaction was not obviously affected by decreasing the concentration of gold, but was greatly retarded by decreasing that of  $\text{H}_2\text{O}_2$ . These sols, when dilute, are amicronic and stable.

**Reaction with Ozone.**—Ozonised oxygen was passed at room temperature through  $\text{Au}_2\text{S}_3$  sol containing 0.01 mg. Au per c.c. The sol slowly (20 mins.) turned pink, and finally became bluish-purple. The Tyndall effect, which was very faint, indicated that the blue colour was due neither to the production of large particles nor to coagulation. When boiled for 2 minutes the sol became pure red. Similar behaviour has been noticed in sols prepared by reduction methods, when the reduction has been incomplete, and in such cases the blue or purple colour is usually attributed to a gold oxide. This explanation is supported by the observation that a red gold sol made by the phosphine method was turned purple by passing ozonised oxygen through it; the red colour was regained on boiling, and the Tyndall effect remained unchanged throughout.

### Particle Concentration in Sulphide Sols.

The particles in gold sulphide sols cannot be directly counted. Their size decreases with increasing dilution of the parent solutions, the largest "equivalent gold particle" (*i.e.* one containing the same amount of gold as the sulphide particles) having a radius of  $2.5 \mu\mu$ . The particles are, therefore, too small to count in the ultramicroscope, and must be grown before their number or size can be determined. It has been shown already that gold sulphide reacts rather slowly with potassium chloroaurate; it seems probable that the slowness is due entirely to the solid reaction, and that the surface of the particle is converted into gold very quickly. This view is borne out by the observation that the sulphide particles behave exactly like gold nuclei when an attempt is made to grow them by reducing a chloroaurate solution in their presence with hydroxylamine. Table I gives the results of determining in this manner the number of sulphide particles per c.c. in five different sols of concentration varying from 0.08 to 0.0008 mg. Au per c.c. The measurements were made by the method described in Part I of this series.<sup>8</sup> The first column gives the relative dilution of the particular sol used, and the second the calculated number of nuclei in the undiluted sol. These numbers should not vary with dilution if the sulphide particles do in fact act as the sole nuclei of condensation; if, on the other hand, the number of gold particles produced depends on some other factor, the observed numbers would be constant, and the calculated numbers would therefore be directly proportional to the dilutions.

TABLE I.

( $c$  = Au per c.c. of undiluted  $\text{Au}_2\text{S}_3$  sol;  $v$  = relative dilution;  $n$  = number of particles per c.c. of undiluted sol.)

$c = 0.08 \text{ mg./c.c.}$		$c = 0.02 \text{ mg./c.c.}$		$c = 0.01 \text{ mg./c.c.}$	
$v$	$n$	$v$	$n$	$v$	$n$
1.0	$6.0 \times 10^{13}$	1.0	$3.3 \times 10^{13}$	1.0	$2.6 \times 10^{13}$
1.5	$5.6 \times 10^{13}$	1.025	$3.2 \times 10^{13}$	1.33	$2.6 \times 10^{13}$
2.0	$6.7 \times 10^{13}$	1.47	$3.4 \times 10^{13}$	1.67	$2.5 \times 10^{13}$
2.5	$6.8 \times 10^{13}$	1.5	$3.0 \times 10^{13}$	2.0	$2.4 \times 10^{13}$
		2.0	$2.8 \times 10^{13}$		
		2.2	$2.9 \times 10^{13}$		

$c = 0.004 \text{ mg./c.c.}$		$c = 0.0008 \text{ mg./c.c.}$	
$v$	$n$	$v$	$n$
1.0	$1.3 \times 10^{13}$	1.0	$5.0 \times 10^{12}$
1.25	$1.4 \times 10^{13}$	1.4	$4.3 \times 10^{12}$
1.75	$1.1 \times 10^{13}$	2.0	$4.5 \times 10^{12}$
2.5	$1.1 \times 10^{13}$	3.0	$4.5 \times 10^{12}$

The tabulated figures show that the number of gold particles formed, in each of the five sols, is proportional to the amount of sulphide sol used; it may therefore be assumed that this number is also that of the sulphide

<sup>8</sup> Usher, *Trans. Faraday Soc.*, 1938, **34**, 1230.

particles present. The average deviation from the mean, averaged for the five sols, is 6.2 %, which is well within the permissible experimental error.

### Particle Concentration in Gold Sols derived from Sulphide Sols.

Theoretically any one of the four oxidising agents previously named could be used to convert the sulphide sols into gold sols with a view to comparing their particle concentrations. In practice only hydrogen peroxide has been found satisfactory, since sols made with the others show too great a tendency to coagulate spontaneously. The sulphide sol containing 0.02 mg. Au per c.c. was converted into a gold sol by boiling some of the diluted sol with very dilute hydrogen peroxide. The original sol had particles of equivalent radius 2.0  $\mu$ . When the conversion into gold was complete the resulting sol was suitably diluted, the particles were grown, and the size of the nuclei determined in the usual way. The results of two series of such measurements are in Table II.

TABLE II.

Relative Dilution.	Particle Radius.	Relative Dilution.	Particle Radius.
1.0	2.0 $\mu$	1.0	2.0 $\mu$
1.43	2.0	1.5	2.1
2.14	2.2	2.0	2.1

It is seen from these measurements that when a gold sulphide sol is oxidised by hydrogen peroxide to form a gold sol, the amount of gold in each particle, and consequently the number of particles, remains unchanged. It is difficult to imagine that this could happen unless each sulphide particle is converted into a gold particle by the removal of sulphur; and although no such proof is possible when the other oxidising agents are used, there is no reason to assume a different mechanism of conversion in their case.

### Conclusion.

In all the methods of making nuclear sols examined, the chemical reaction leading to the formation of gold has been found to occur in at least two stages; the first is the formation of nuclei containing other elements besides gold; the second stage consists in the removal of these elements from the particles, leaving gold. Nothing definite is known about the reactions of gold salts with reducing agents such as hydrazine and hydroxylamine, which do not form nuclear sols; there is no evidence at present that insoluble particles, other than gold, are formed in them at any stage. With such non-nuclear reducing agents the formation of colloidal gold is apparently more rapid than it is with nuclear reducing agents (*e.g.* phosphorus, phosphine, hydrogen sulphide), but it may be surmised that the reactions which produce the first insoluble particles (gold) in the former case are slower than those which produce the first insoluble particles (auric phosphide, auric sulphide) in the latter. In the one reaction that permits exact investigation the number of the resulting gold particles has been shown to be determined by that of the antecedent nuclei, and it is reasonable to suppose that this will be true of all reactions of a similar kind in which the final gold-

producing reaction is topochemical. This would imply that the number and size of colloidal gold particles are independent of the velocity of the final reaction by which the metal is produced, but are determined rather by the velocity of that reaction which first produces an insoluble substance. The reaction between a gold salt and hydrogen sulphide is ionic, and instantaneous in the sense that every encounter between the reacting molecules is effective; if this is true also of the reactions with phosphorus and phosphine, the difference in size between the particles produced by the nuclear and non-nuclear types of reducing agent is seen to be in harmony with the generally recognised relation between crystal size and degree of supersaturation.

### Summary.

1. The reduction of gold salts by phosphine and by hydrogen sulphide under certain conditions leads to the formation of nuclear gold sols. Under other conditions these reactions may give rise to sols of auric phosphide and auric sulphide, the properties of which are described.

2. The reactions of gold salts with phosphorus in ether (Faraday's method), phosphine, and hydrogen sulphide occur in at least two stages, one of which consists in the formation of an insoluble gold compound, and the last of which consists in a topochemical conversion of this into gold.

3. It is suggested that the difference in the size of gold particles produced by nuclear and non-nuclear types of reducing agent is determined by the speed of the reaction which first produces an insoluble substance, rather than by the overall speed of the complete process.

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## THE INFLUENCE OF INTERFACIAL CURVATURE ON SOLUBILITY.

BY R. STEVENSON BRADLEY.

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If curvature occurs at the interface between two liquids, then, as is well known, the solubility is altered. It is of interest to consider the behaviour in the light of a change in energy due to molecular interaction without referring explicitly to the surface pressure due to curvature. The change in energy arises owing to the difference in molecular environment between a molecule at a plane and curved surface, and the method has the advantage that the enquiry can be pursued down to very small droplets. With such droplets, *e.g.* those which form on nuclei, there is considerable doubt as to the applicability of Kelvin's equation. The results apply not only to the solubility of liquids in liquids, but also to the condensation of vapours on nucleating particles or in capillary systems.

Suppose that we have a sphere of liquid A of radius  $r$  containing  $q_A$  molecules per c.c., immersed in a liquid B containing  $q_B$  molecules

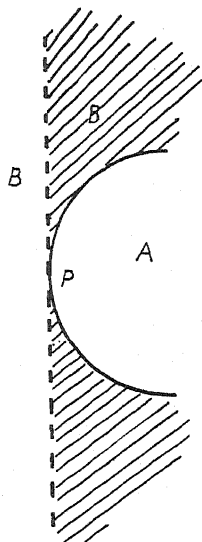


FIG. 1.

per c.c. Let the law of force between two molecules of A be of the form  $\frac{\lambda_n}{x^n} - \frac{\lambda_m}{x^m}$ , and between a molecule of A and one of B be  $\frac{\lambda_v}{x^v} - \frac{\lambda_u}{x^u}$ . Consider a molecule of A at the surface of the sphere at P, Fig. 1. Then the difference in energy of this molecule when the interface is plane and when it is curved is given by  $E_A - E_B$ , where  $E_A$  is the energy of a molecule at P due to the shaded portion filled with A, and  $E_B$  that due to the shaded portion filled with B. The shaded region is supposed to extend round the sphere to  $\infty$  except for the dotted boundary. This energy can be accurately expressed.

The potential of a molecule distant  $c$  from the centre of a sphere of radius  $r$  is, in absolute value,<sup>1</sup>

$$\theta(m) - \theta(n) = \frac{2\pi q \lambda_m}{c(m-1)(m-3)} \left[ \frac{1}{(m-5)(c+r)^{m-5}} - \frac{c}{(m-4)(c+r)^{m-4}} - \frac{1}{(m-5)(c-r)^{m-5}} + \frac{c}{(m-4)(c-r)^{m-4}} \right] - \theta(n), \quad (1)$$

where  $\theta(n)$  is obtained by replacing  $m$  by  $n$  in  $\theta(m)$ .

In our problem  $c$  may be put equal to  $r + d$ , where  $d$  is the molecular diameter, giving the energy, due to the sphere A,

$$\beta(m) - \beta(n) = \frac{2\pi q_A \lambda_m}{(r+d)(m-1)(m-3)} \left[ \frac{1}{(m-5)(d+2r)^{m-5}} - \frac{1}{(m-4)(d+2r)^{m-4}} - \frac{1}{(m-5)d^{m-5}} + \frac{1}{(m-4)d^{m-4}} \right] - \beta(n) \quad (2)$$

where  $\beta(n)$  is obtained by replacing  $m$  by  $n$  in  $\beta(m)$ .

Now the energy of a molecule at the surface of an infinite plane with liquid extending to infinity underneath is

$$\gamma(m) - \gamma(n) = \frac{2\pi q_A \lambda_m}{(m-1)(m-3)(m-4)d^{m-4}} - \gamma(n),$$

where  $\gamma(n)$  is obtained by replacing  $m$  by  $n$  in  $\gamma(m)$ . Hence

$$E_A/q_A = f(m) - f(n) = \frac{2\pi \lambda_m}{(r+d)(m-1)(m-3)} \left[ \frac{1}{(m-4)(m-5)d^{m-5}} - \frac{1}{(m-5)(d+2r)^{m-5}} + \frac{(r+d)}{(m-4)(d+2r)^{m-4}} \right] - f(n), \quad (3)$$

where  $f(n)$  is obtained by replacing  $m$  by  $n$  in  $f(m)$ .

Similarly

$$E_B/q_B = f(u) - f(v) \text{ and } E_A/q_A - E_B/q_B = f(m) - f(n) - f(u) + f(v). \quad (4)$$

When  $r \gg d$ ,

$$E_A/q_A - E_B/q_B = \phi(m) - \phi(n) - \phi(u) + \phi(v),$$

where  $\phi(m) = \frac{2\pi}{r} \frac{\lambda_m}{(m-1)(m-3)(m-4)(m-5)d^{m-5}}.$

But the interfacial energy of A is given by<sup>2</sup>

$$\sigma_A = \frac{N^2 \rho_A^2}{M_A^2} \left[ \frac{\lambda_m}{(m-1)(m-3)(m-4)(m-5)d^{m-5}} - \frac{\lambda_n}{(n-1)(n-3)(n-4)(n-5)d^{n-5}} \right] \quad (5)$$

<sup>1</sup> Bradley, *Phil. Mag.*, 1932, 13, 853: cf. equation above fig. 2.

<sup>2</sup> *Ibid.*, 1931, 11, 846.



where  $N$  is Avogadro's number,  $\rho_A$  is the density of A and  $M_A$  its molecular weight, *i.e.*

$$q_A = \frac{\rho_A N}{M_A}.$$

$$\text{Hence} \quad E_A - E_B = \frac{2\pi}{rN} (\sigma_A M_A / \rho_A - w M_A / \rho_A),$$

where  $w$  is the work of adhesion, *i.e.*  $w = \sigma_A + \sigma_B - \sigma_{AB}$ , and the energy difference per g. mol.

$$E = \frac{2\pi}{r} \frac{M_A}{\rho_A} (\sigma_{AB} - \sigma_B) \quad . \quad . \quad . \quad (6)$$

If the osmotic work of transference of a differential element from the droplet to a plane surface be equated to the surface work we obtain in the usual way an increase in solubility ( $S$ ) given by  $S = S_0 e^{E/RT}$ , where  $S_0$  is the solubility over a plane and  $S$  that over a sphere of radius  $r$ .

$$\text{Hence} \quad \log \frac{S}{S_0} = \frac{2\pi}{RT} \frac{M_A}{r \rho_A} (\sigma_{AB} - \sigma_B) \quad . \quad . \quad . \quad (7)$$

which is identical with Kelvin's result except for the second term, which is usually small, *e.g.* for a liquid volatilising into a vacuum.

This derivation has the advantage that it is possible to estimate exactly (if the premises are correct) the divergence from the formula when  $r$  is small. For solid crystalline particles, however, for which it is often applied there is no justification for the application, owing to the existence of edges and corners, in fact strictly speaking the energy of activation varies continuously over a crystalline face of a small solid particle.

In order to estimate the extent of divergence for very small droplets we may neglect the repulsive terms and put  $m = u = 7$ , the value given by wave mechanics. Then when  $r = 10d$  formulæ (6) gives a value only 7.6 % in excess of the true result obtained from equation (3), and when  $r = 5d$  the excess is only 12.9 %. The same remarks apply to the vapour pressure of a droplet.

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## THE MOLECULAR STATE OF INORGANIC LIQUIDS.

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Although the osmotic properties of inorganic substances in aqueous solution have been the subject of extensive investigation, few measurements have been made upon non-aqueous solutions of non-polar and dipolar inorganic compounds. In connection with other investigations in this laboratory we were led to examine the properties of arsenic trichloride, phosphorus trichloride, sulphur monochloride, phosphorus oxychloride, sulphuryl chloride and thionyl chloride for the purpose of ascertaining the molecular condition of these substances in non-polar

media. Inasmuch as the ebullioscopic measurements of previous workers<sup>1</sup> led to erroneous results owing to the volatility of the solute, the cryoscopic method was employed in the present determinations.

### Experimental.

Since the liquids suffer ready hydrolysis on exposure to the atmosphere they were allowed to stand for a short time over freshly activated silica gel (in order to adsorb traces of free hydrogen chloride) prior to distillation in an all-glass apparatus, which incorporated a long Dufton column and

TABLE I.

Substance.	Weight of Solute (g.).	Depression.	Molecular Weight.
Arsenic trichloride $M = 181.3$	0.583	0.96	180
	1.214	1.97	182
	0.445	0.72	182
	0.986	1.58	184
			Mean 182
Phosphorus trichloride $M = 137.4$	0.308	0.60	152
	0.664	1.31	150
	1.175	2.31	150
	1.006	2.01	148
	1.389	2.73	150
Sulphur monochloride $M = 135.0$			Mean 150
	0.730	1.55	139
	0.983	2.07	140
	0.369	0.80	136
	0.885	1.90	137
Phosphorus oxychloride $M = 153.4$	1.434	3.06	138
			Mean 138
	0.223	0.39	169
	0.623	1.09	169
	0.958	1.70	167
Sulphuryl chloride $M = 135.1$	0.481	0.89	160
	1.187	2.15	163
			Mean 166
	1.079	2.26	141
	1.367	2.82	143
Thionyl chloride $M = 119.1$	0.442	0.95	137
	0.702	1.49	139
			Mean 140
	0.246	0.56	130
	0.610	1.41	127
	1.060	2.45	128
	0.765	1.88	120
	1.310	3.16	122
			Mean 125

condensing unit provided with guard-tubes of anhydrous calcium chloride and silica gel. Each liquid was subjected to at least three fractionations under ordinary pressure, but sulphur monochloride was fractionated under reduced pressure in order to avoid thermal decomposition. The boiling-points and densities of the pure liquids were as follows: arsenic trichloride, b.p.  $129.0^\circ/771$  mm.,  $d_4^{25}$  2.1497; phosphorus trichloride, b.p.  $75.7^\circ/758$  mm.,  $d_4^{25}$  1.5659; sulphur monochloride, b.p.  $42.0^\circ/23$  mm.,  $d_4^{25}$  1.6714; phosphorus oxychloride, b.p.  $105.9^\circ/762$  mm.,  $d_4^{25}$  1.6676; thionyl

<sup>1</sup> Oddo and Serra, *Gazz. Chim. Ital.*, 1899, 31, 222.

chloride, b.p.  $76.5^{\circ}/766$  mm.,  $d_4^{25}$  1.6290; sulphuryl chloride, b.p.  $69.2^{\circ}/754$  mm.,  $d_4^{25}$  1.6570. Benzene (purified for molecular weight determinations) was distilled over phosphorus pentoxide (free from trioxide) before use as solvent.

The cryoscopic apparatus consisted of a Beckmann tube provided with a three-holed rubber stopper carrying a calibrated thermometer, a delivery tube for the admission of nitrogen, and a glass stirrer. The stirrer was arranged to operate through an air-tight device, while a slow stream of rigorously dried nitrogen was passed through the apparatus. The gas was led out through the side-tube of the Beckmann vessel, which was also fitted with a guard-tube of calcium chloride to prevent backward diffusion of moisture. The measurements were carried out in accordance with the orthodox procedure with due regard to the precautions adopted in the case of highly reactive solutions.<sup>2</sup> The final concentrations employed, however, were rather higher than is customary in cryoscopic work in order to detect, if possible, the incidence of association. The cryoscopic constant of benzene was determined from the depressions produced by pure naphthalene under the same experimental conditions. The mean value,  $K = 52.3$ , was employed in calculating the results shown in Table I.

### Discussion.

The molecular state of the pure liquids has been studied by Vaubel,<sup>3</sup> but as may be seen from Table II, the values of the association factor

TABLE II.—ASSOCIATION FACTORS.

	Vaubel.	Ramsay and Shields.	Walden.	Longinescu.	Present Work.
AsCl <sub>3</sub> . . . .	1.50	—	0.83	0.83	1.00
PCl <sub>3</sub> . . . .	1.48	1.02	0.97	1.17	1.09
S <sub>2</sub> Cl <sub>2</sub> . . . .	1.37	0.95	1.27	1.44	1.02
POCl <sub>3</sub> . . . .	—	1.00	0.99	0.99	1.08
SOCl <sub>2</sub> . . . .	—	1.08	0.80	1.09	1.05
SO <sub>2</sub> Cl <sub>2</sub> . . . .	—	0.97	1.09	0.80	1.03

obtained by this investigator are higher than would be anticipated from the general properties of the liquids. The association factors calculated from the surface energy equations of Ramsay and Shields<sup>4</sup> and Walden<sup>5</sup> are in good agreement in the case of all the liquids with the exception of sulphur monochloride. The values computed from the empirical equation of Longinescu<sup>6</sup> correspond fairly well with those obtained by the other methods.

The cryoscopic measurements show that the observed molecular weight does not change appreciably with the concentration of the solution. Although the calculation of the association factors on this basis depends on the premise that no interaction occurs between solvent and solute, there is little doubt that these values are more reliable than those calculated from the surface energy relations. In fact, we find no discrepancy in the case of sulphur monochloride, which behaves as a perfectly normal liquid. The depressions produced by phosphorus

<sup>2</sup> Bowden, *J. Chem. Soc.*, 1939, 37.

<sup>3</sup> Vaubel, *J. prak. Chem.*, 1904, 69, 138.

<sup>4</sup> Ramsay and Shields, *J. Chem. Soc.*, 1893, 63, 1087.

<sup>5</sup> Walden, *Z. physik. Chem.*, 1909, 65, 129.

<sup>6</sup> Longinescu, *J. Chim. physique*, 1903, 1, 289.

trichloride and phosphorus oxychloride are slightly lower than the ideal, and these deviations may be due to internal pressure differences between solvent and solute or to slight association of the solute.

It has been found by Sugden and his co-workers<sup>7</sup> that the parachor of several of the above substances is independent of the temperature of measurement and that these liquids, therefore, are essentially normal. Moreover, measurements in this laboratory reveal that the variation of viscosity with temperature conforms to the Andrade exponential formula<sup>8</sup> in the case of arsenic trichloride, sulphur monochloride and phosphorus oxychloride. Although such conformity does not in itself prove that association is absent, it does imply that there is no change of association with temperature. In the case of phosphorus trichloride, sulphuryl chloride and thionyl chloride, however, there is appreciable departure from the exponential relation, and this is doubtless to be referred to the difference in the associative tendency of the molecules at different temperatures.

### Summary.

Molecular weight determinations on non-polar and dipolar inorganic chlorides in benzene solution indicate that the liquids behave as normal solutes with the exception of phosphorus trichloride and phosphorus oxychloride which show slight deviations from ideality. The results are briefly discussed in the light of the various formulæ for calculating association factors, and also from the standpoint of the exponential formula for the variation of viscosity with temperature.

<sup>7</sup> Sugden, Reed and Wilkins, *J. Chem. Soc.*, 1925, 127, 1525.

<sup>8</sup> Andrade, *Phil. Mag.*, 1934, 17, 497, 698.

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## THE THERMODYNAMICS OF INTERFACES IN SYSTEMS OF SEVERAL COMPONENTS.

By E. A. GUGGENHEIM, M.A., Sc.D.

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### Part I. Plane Interfaces.

#### 1. Introduction.

The thermodynamics of an interface separating a simple liquid from its vapour offer little difficulty and are well known. The physical chemist's interest, however, is directed largely to variations of composition. The thermodynamical formulæ for an interface separating a solution from its vapour or for an interface separating two liquid phases of at least two components are considerably more complicated. The classical treatment is, of course, that of Gibbs,<sup>1</sup> and it has the mathematical elegance characteristic of all Gibbs' work, but it must be admitted that this treatment is not readily assimilated. The characteristic feature of Gibbs' treatment is the introduction of a mathematical surface. Each extensive property of the system, such as its free energy, its entropy, its content of each component, is then imagined to be composed of three

<sup>1</sup> Gibbs, *Collected Works*, vol. I, pp. 219 *seq.* (Longmans, 1928).

parts: the first is the contribution of the one bulk phase on the supposition that its properties remained homogeneous as far as the mathematical surface; the second is the similar contribution of the other bulk phase; the residual part of the extensive property is assigned to the mathematical surface. Thus to the mathematical surface are assigned a free energy, an entropy, a quantity of each component, but of course no volume. Although this method of treatment is mathematically accurate it has two features, closely related to each other, which make it particularly difficult to visualise. The first is that the actual values of the several extensive properties assigned to the mathematical surface depend to a marked degree on the exact position of the mathematical surface in the physical interfacial layer. In fact the mathematical surface can be so placed as to make a selected one of these extensive properties have an arbitrarily chosen value, such as zero.<sup>2</sup> The second unnatural feature is that the mathematical surface having by definition no volume, does not correspond to our physical picture of an interfacial layer. Experience indicates that it is much less difficult to use Gibbs' formulæ than to understand them.

In contrast to Gibbs' abstract treatment of surfaces, several Dutch physicists, notably Van der Waals and Bakker,<sup>3</sup> have made important contributions to the theory of surfaces by treating the surface as a layer of small but finite uniform thickness. Their treatment applies to a system of a single component, that is to the surface separating a simple liquid from its vapour. Verschaffelt<sup>4</sup> has supplied a treatment of surfaces between phases of several components, which explicitly recognises the finite thickness of the surface layer. This treatment shares the elegance of Gibbs' analysis, while avoiding the abstraction of his mathematical surface. The present treatment agrees in principle with that of Verschaffelt, but differs from it particularly in my choice of a set of independent variables, which I believe to be convenient in practice. In Part I, following Verschaffelt, I shall suppose the interface to be plane. In Part II I shall discuss briefly the applicability of the formulæ to curved interfaces.

## 2. Definitions.

Fig. 1 represents two homogeneous bulk phases,  $\alpha$  and  $\beta$ , between which lies the surface layer  $\sigma$ . The boundary between  $\sigma$  and  $\alpha$  is the

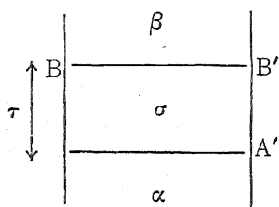


FIG. 1.

plane  $AA'$ , that between  $\sigma$  and  $\beta$  the parallel plane  $BB'$ . All properties of  $\sigma$  are uniform in directions parallel to  $AA'$ , but not in the direction normal to  $AA'$ . At and near  $AA'$  the properties are identical with those of the phase  $\alpha$ ; at and near  $BB'$  they are identical with those of the phase  $\beta$ . Subject to these conditions there is freedom of choice in placing the planes  $AA'$  and  $BB'$ . It will be possible and therefore natural, though not essential, so to place the planes  $AA'$  and  $BB'$  that the uniform distance between them is sub-microscopic and usually less than  $10^{-6}$  cm.

<sup>2</sup> See Guggenheim and Adam, *Proc. Roy. Soc. A*, 1933, **139**, 218.

<sup>3</sup> See *Handb. Experimentalphysik*, 1928, **6**.

<sup>4</sup> Verschaffelt, *Acad. roy. Belgique, Bull. classe sciences*, 1936, **22**, No. 4, pp. 373, 390, 402.

Since the surface layer  $\sigma$  is a material system with a well-defined volume and material content, its thermodynamic properties require no special definition. We may speak of its temperature, free energy, composition and so on just as for a homogeneous bulk phase. The only functions that call for special comment are the pressure and the surface tension. In any homogeneous bulk phase the force across any unit area is equal in all directions and is called the pressure. But in  $\sigma$  the force across unit area is not the same in all directions. If, however, we choose any plane of unit area parallel to  $AA'$  and  $BB'$ , then the force across it has the same value for all positions of the plane whether it lie in  $\alpha$ ,  $\beta$  or  $\sigma$ ; this value of the force across unit area is called the pressure  $P$ . Suppose, on the other hand, we choose a plane perpendicular to  $AA'$  and extending above  $AA'$  and below  $BB'$ ; let this plane have the form of a rectangle of height  $h$  (parallel to  $AB$ ) and of thickness  $l$  (perpendicular to the plane of the paper). Then the force across this plane will be equal to  $Phl - \gamma l$ , where  $P$  is the above-defined pressure and  $\gamma$  is the interfacial tension. If the height of this plane is chosen to extend exactly from  $AA'$  to  $BB'$ , then the force across it will be equal to  $P\tau l - \gamma l$ , if the height  $AB$  is denoted by  $\tau$ . Let the surface layer have an area  $A$ , a perimeter  $s$  and a volume  $V^\sigma$  so that

$$V^\sigma = \tau A. \quad (2,1)$$

Suppose the area to be increased to  $A + dA$ , the perimeter to  $s + ds$ , the thickness to  $\tau + d\tau$  and the volume to  $V^\sigma + dV^\sigma$ , the *material content remaining unaltered*. Then the work done on  $\sigma$  consists of  $-pAd\tau$  by the forces across  $AA'$  and  $BB'$  and  $-(P\tau s - \gamma s)dA/s$  by the forces parallel to the planes  $AA'$  and  $BB'$ . The total work done on  $\sigma$  is therefore

$$\begin{aligned} & -PAd\tau - (P\tau s - \gamma s)dA/s \\ & = -P(Ad\tau + \tau dA) + \gamma dA \\ & = -PdV^\sigma + \gamma dA. \end{aligned} \quad (2,2)$$

This expression takes the place of  $-PdV^\alpha$  for a homogeneous bulk phase  $\alpha$ .

### 3. Free Energy of Surface Layer.

For the most general variation of the free energy  $F^\alpha$  of a homogeneous bulk phase we have the well-known formula

$$dF^\alpha = -S^\alpha dT - PdV^\alpha + \sum_r \mu_r dn_r^\alpha, \quad (3,1)$$

where  $S$  denotes entropy,  $T$  temperature,  $P$  pressure,  $V$  volume,  $\mu_r$  chemical potential of the component  $r$ , and  $n_r$  number of moles of component  $r$ . The first term on the right gives the dependence of  $F$  on temperature, the second its dependence on volume and the remaining terms its dependence on composition. For a surface phase  $\sigma$  the dependence of the free energy  $F^\sigma$  on the temperature and the composition will be exactly parallel to that for a bulk phase; this may be taken as practically the definition of entropy and chemical potentials. But for the dependence of  $F^\sigma$  on size and shape we must replace  $-PdV$  by the expression (2, 2). We thus obtain the formula

$$dF^\sigma = -S^\sigma dT - PdV^\sigma + \gamma dA + \sum_r \mu_r dn_r^\sigma. \quad (3,2)$$

There is no need to add superscripts to  $T$ ,  $P$ ,  $\mu_r$ , because these must have values uniform throughout  $\alpha$ ,  $\beta$  and  $\sigma$  in order that there may be thermal, mechanical and physico-chemical equilibrium.

#### 4. Analogue of Gibbs-Duhem Relations.

In formula (3, 2) let us now set

$$dT = 0, \quad dV^\sigma = -V^\sigma d\lambda, \quad dA = -Ad\lambda, \quad dn_r^\sigma = -n_r^\sigma d\lambda, \quad (4, 1)$$

and obtain

$$dF^\sigma = -d\lambda(-PV^\sigma + \gamma A + \sum_r \mu_r n_r^\sigma). \quad (4, 2)$$

This substitution corresponds physically to decreasing the extent of the surface layer  $\sigma$  by simply cutting off a portion at its edge, so that what remains is exactly like the original system except that it is reduced in extent in the ratio  $(1 - d\lambda) : 1$ . It is therefore obvious that  $F^\sigma$  will also be reduced in the same ratio. It is equally obvious that  $P, \gamma, \mu_r$  remain unaltered. (In mathematical terminology: at constant temperature and thickness  $F^\sigma$  is homogeneous of first degree in  $V^\sigma, A$  and  $n_r^\sigma$  and of zero degree in  $P, \gamma, \mu_r$ .) Thus the conditions (4, 1) imply the simultaneous conditions

$$dF^\sigma = -F^\sigma d\lambda, \quad dP = 0, \quad d\gamma = 0, \quad d\mu_r = 0. \quad (4, 3)$$

Substituting the value of  $dF^\sigma$  into (4, 2) we obtain

$$-F^\sigma d\lambda = -(-PV^\sigma + \gamma A + \sum_r \mu_r n_r^\sigma) d\lambda, \quad (4, 4)$$

and equating coefficients of  $d\lambda$

$$F^\sigma = -PV^\sigma + \gamma A + \sum_r \mu_r n_r^\sigma \quad (4, 5)$$

or

$$F^\sigma + PV^\sigma - \gamma A = \sum_r \mu_r n_r^\sigma. \quad (4, 6)$$

(Alternatively formula (4, 6) can be derived mathematically from (3, 1) by using Euler's theorem.) Formula (4, 6) is the analogue of

$$F^\alpha + PV^\alpha = \sum_r \mu_r n_r^\alpha \quad (4, 7)$$

for a homogeneous bulk phase.

If we define the Gibbs functions  $G^\alpha$  and  $G^\sigma$  by

$$G^\alpha = F^\alpha + PV^\alpha, \quad (4, 8)$$

$$G^\sigma = F^\sigma + PV^\sigma - \gamma A, \quad (4, 9)$$

then we deduce from (3, 1) and (4, 6)

$$dG^\sigma = -S^\sigma dT + V^\sigma dP - Ad\gamma + \sum_r \mu_r dn_r^\sigma, \quad (4, 10)$$

$$G^\sigma = \sum_r \mu_r n_r^\sigma. \quad (4, 11)$$

These two formulæ are the analogues of the formulæ

$$dG^\alpha = -S^\alpha dT + V^\alpha dP + \sum_r \mu_r dn_r^\alpha, \quad (4, 12)$$

$$G^\alpha = \sum_r \mu_r n_r^\alpha. \quad (4, 13)$$

for a homogeneous bulk phase. Thus the partial molar derivatives of  $G^\alpha$  are the  $\mu_r^\alpha$ 's and the partial molar derivatives of  $G^\sigma$  are the  $\mu_r^\sigma$ 's.

If we differentiate (4, 6) we obtain

$$dF^\sigma + PdV^\sigma + V^\sigma dP - \gamma dA - Ad\gamma = \sum_r \mu_r dn_r^\sigma + \sum_r n_r^\sigma d\mu_r. \quad (4, 14)$$

If we subtract (4, 14) from (3, 1) we obtain

$$S^\sigma dT - V^\sigma dP + Ad\gamma + \sum_r n_r^\sigma d\mu_r = 0, \quad (4, 15)$$

which is the analogue of the Gibbs-Duhem formula

$$S^\sigma dT - V^\sigma dP + \sum_r n_r^\sigma d\mu_r = 0. \quad (4, 16)$$

If we divide (4, 16) throughout by  $A$  we obtain the more convenient form

$$s^\sigma dT - \tau dP + d\gamma + \sum_r \Gamma_r d\mu_r = 0, \quad (4, 17)$$

where  $s^\sigma$  is the entropy per unit area and  $\Gamma_r$  is the number of moles, of the component  $r$  in unit area of surface layer, defined respectively by

$$s^\sigma = S^\sigma/A, \quad \Gamma_r = n_r^\sigma/A. \quad (4, 18)$$

It will be remembered that  $\tau$  is the thickness of the surface layer, that is to say the length AB in Fig. 1.

### 5. Independent Variables.

We can rewrite (4, 17) in the form

$$-d\gamma = s^\sigma dT - \tau dP + \sum_r \Gamma_r d\mu_r. \quad (5, 1)$$

This tells us how the interfacial tension varies when the temperature, pressure and chemical potentials vary, but these variables are not all independently variable. It will be more useful if we can obtain a formula for  $d\gamma$  expressed in terms of independent variables.

The state of a single homogeneous bulk phase (apart from its quantity) may be completely defined by its temperature  $T$ , its pressure  $P$ , and its composition. If there are  $r$  components, the composition is conveniently defined by the  $r$  mole fractions  $x_r$  of which only  $r - 1$  are independent because of the identity

$$\sum_r x_r = 1. \quad (5, 2)$$

Alternatively the state of the single phase might be defined by the  $r + 2$  quantities  $T$ ,  $P$ ,  $\mu_r$  of which only  $r + 1$  are independent because of the Gibbs-Duhem relation (4, 16).

If we have two homogeneous phases  $\alpha$  and  $\beta$  of  $r$  components, then the state of each separately may be defined by the variables  $T$ ,  $P$ ,  $x_2, x_3, \dots, x_r$ . If the two phases are in equilibrium there will be one condition of thermal equilibrium (equality of  $T^\alpha$  and  $T^\beta$ ), one condition of mechanical equilibrium (equality of  $P^\alpha$  and  $P^\beta$ ), and  $r$  conditions of chemical equilibrium (equality of  $\mu_r^\alpha$  and  $\mu_r^\beta$ ), one for each component. Thus the number of independent variables is reduced from  $2(r + 1)$  to  $2(r + 1) - (r + 2)$  or  $r$ . We may, for example, take these to be  $T$ ,  $x_2^\alpha, x_3^\alpha, \dots, x_r^\alpha$ , in which case  $P$  is not an independent variable.

Let us now return to our original system consisting of the two bulk phases  $\alpha$  and  $\beta$  and the surface layer  $\sigma$ . At equilibrium all the properties of the surface layer  $\sigma$  other than its extent are determined by the states of the phases  $\alpha$  and  $\beta$ . Thus the number of independent variables for the whole system is  $r$ , and these can be taken as  $T$ ,  $x_2^\alpha, x_3^\alpha, \dots, x_r^\alpha$ . Thus only  $r$  out of the  $r + 2$  differentials on the right of (5, 1) are independent. It must therefore be possible to eliminate  $dP$  and one other.

We must remember that the present treatment is confined to plane surface layers. If we allowed curved surfaces, there would no longer be equality of  $P^\alpha$  and  $P^\beta$ , and so we should have an extra degree of freedom.



### 6. Special Notation.

At this stage it is convenient for the sake of brevity to introduce a special notation. Suppose  $\phi^\alpha$  to be any intensive property of the phase  $\alpha$ . Then we may regard  $\phi^\alpha$  as a function of  $T, P, x_2^\alpha, x_3^\alpha, \dots, x_r^\alpha$ . We shall now introduce the operator  $D$  defined as follows:

$$D\phi^\alpha = \frac{\partial \phi^\alpha}{\partial x_2} dx_2^\alpha + \frac{\partial \phi^\alpha}{\partial x_3} dx_3^\alpha + \dots + \frac{\partial \phi^\alpha}{\partial x_r} dx_r^\alpha, \quad (6, 1)$$

so that 
$$d\phi^\alpha = \frac{\partial \phi^\alpha}{\partial T} dT + \frac{\partial \phi^\alpha}{\partial P} dP + D\phi^\alpha. \quad (6, 2)$$

In words  $D\phi^\alpha$  is the part of the variation of  $\phi^\alpha$  due to variation of composition when  $T, P$  are kept constant.

When we use this notation we have

$$d\mu_r^\alpha = -s_r^\alpha dT + v_r^\alpha dP + D\mu_r^\alpha, \quad (6, 3)$$

where  $s_r^\alpha, v_r^\alpha$  are the partial molar entropy and the partial molar volume of  $r$  in the phase  $\alpha$ . Similarly in the phase  $\beta$  we have

$$d\mu_r^\beta = -s_r^\beta dT + v_r^\beta dP + D\mu_r^\beta. \quad (6, 4)$$

Using this same notation, we can write the Gibbs-Duhem relations in the forms

$$\sum_r x_r^\alpha D\mu_r^\alpha = 0, \quad (6, 5)$$

$$\sum_r x_r^\beta D\mu_r^\beta = 0. \quad (6, 6)$$

### 7. Transformation of Formulæ.

The variation of the chemical potential of each component  $r$  in the phases  $\alpha$  and  $\beta$  are determined by (6, 3) and (6, 4) respectively. The conditions for physico-chemical equilibrium between the two phases are of the form

$$\mu_r^\alpha = \mu_r^\beta. \quad (7, 1)$$

Hence for variations at which equilibrium is maintained, we have

$$d\mu_r^\alpha = d\mu_r^\beta. \quad (7, 2)$$

If we multiply (7, 2) by  $x_r^\beta$ , substitute from (6, 3) and (6, 4) and add for all  $r$  we obtain, using (6, 6),

$$-\sum_r x_r^\beta (s_r^\alpha - s_r^\beta) dT + \sum_r x_r^\beta (v_r^\alpha - v_r^\beta) dP + \sum_r x_r^\beta D\mu_r^\alpha = 0. \quad (7, 3)$$

If we substitute from (6, 3) into (5, 1) we obtain

$$-d\gamma = (s^\sigma - \sum_r \Gamma_r s_r^\alpha) dT - (\tau - \sum_r \Gamma_r v_r^\alpha) dP + \sum_r \Gamma_r D\mu_r^\alpha. \quad (7, 4)$$

If we now eliminate  $dP$  between (7, 3) and (7, 4) we obtain

$$\begin{aligned} -d\gamma = & \left\{ (s^\sigma - \sum_r \Gamma_r s_r^\alpha) - (\tau - \sum_r \Gamma_r v_r^\alpha) \frac{\sum_r x_r^\beta (s_r^\alpha - s_r^\beta)}{\sum_r x_r^\beta (v_r^\alpha - v_r^\beta)} \right\} dT \\ & + \sum_r \left\{ \Gamma_r + x_r^\beta \frac{\tau - \sum_r \Gamma_r v_r^\alpha}{\sum_r x_r^\beta (v_r^\alpha - v_r^\beta)} \right\} D\mu_r^\alpha. \end{aligned} \quad (7, 5)$$

This somewhat formidable looking formula can be considerably abbreviated by using a suitable notation. If we denote by  $h^\beta$  the heat absorbed and by  $e^\beta$  the volume expansion when one mole of the phase  $\beta$  is formed reversibly at constant temperature and at constant pressure

by taking the required amounts of the various components from the phase  $\alpha$ , then clearly

$$h^\beta = T \sum_r x_r^\beta (s_r^\beta - s_r^\alpha), \quad (7, 6)$$

$$e^\beta = \sum_r x_r^\beta (v_r^\beta - v_r^\alpha). \quad (7, 7)$$

Similarly, if we denote by  $h^\sigma$  the heat absorbed and by  $e^\sigma$  the volume expansion when unit area of the surface layer  $\sigma$  is formed reversibly at constant temperature and at constant pressure by taking the required amounts of the various components from the phase  $\alpha$ , then clearly\*

$$h^\sigma = T(s^\sigma - \sum_r \Gamma_r s_r^\alpha), \quad (7, 8)$$

$$e^\sigma = \tau - \sum_r \Gamma_r v_r^\alpha. \quad (7, 9)$$

If we use these new symbols, (7, 5) reduces to

$$-d\gamma = \left( h^\sigma - \frac{e^\sigma h^\beta}{e^\beta} \right) \frac{dT}{T} + \sum_r \left( \Gamma_r + \frac{e^\sigma x_r^\beta}{e^\beta} \right) D\mu_r^\alpha. \quad (7, 10)$$

Finally, we can eliminate one of the  $D\mu_r^\alpha$ , say  $D\mu_1^\alpha$ 's, by means of (6, 5). We thus obtain

$$-d\gamma = \left( h^\sigma - \frac{e^\sigma h^\beta}{e^\beta} \right) \frac{dT}{T} + \sum_r' \left\{ \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) + \frac{e^\sigma (x_1^\alpha x_r^\beta - x_r^\alpha x_1^\beta)}{e^\beta x_1^\alpha} \right\} D\mu_r^\alpha, \quad (7, 11)$$

where  $\sum_r'$  denotes that  $r = 1$  is omitted from the summation.

We have now obtained an exact formula expressing  $d\gamma$  in terms of the  $r$  independent variables  $dT$ ,  $D\mu_2^\alpha$ ,  $D\mu_3^\alpha$ , . . .  $D\mu_r^\alpha$ . This formula embraces all the information one can want regarding the variation of the interfacial tension. It will have been noticed that the two bulk phases  $\alpha$  and  $\beta$  have not been treated on a par; formula (7, 11) relates  $d\gamma$  to the  $D\mu_r^\alpha$ , not to the  $D\mu_r^\beta$ . In applications to a liquid-vapour interface it will be usual to take the liquid phase as  $\alpha$ , while in the case of a liquid-liquid interface it is immaterial which of the two liquid phases one takes as  $\alpha$ . From here on it will then be assumed that the phase  $\alpha$  is liquid.

If we denote activity coefficients in the liquid phase  $\alpha$  by  $f_r^\alpha$ , then we have

$$D\mu_r^\alpha = RTD \log x_r^\alpha f_r^\alpha, \quad (7, 12)$$

from which we see that the  $D\mu_r^\alpha$ 's are experimentally measurable quantities. If the vapour phase in equilibrium with the phase  $\alpha$  (this may or may not be the phase  $\beta$ ) may be regarded as a perfect gas and we denote partial vapour pressures over the phase  $\alpha$  by  $p_r^\alpha$ , we also have

$$D\mu_r^\alpha = RTD \log p_r^\alpha. \quad (7, 13)$$

This formula will remain valid even if the vapour is not a perfect gas provided we let  $p_r^\alpha$  denote the fugacities rather than the partial vapour pressures. On this understanding we substitute (7, 13) into (7, 11) and obtain finally

$$-d\gamma = \left( h^\sigma - \frac{e^\sigma h^\beta}{e^\beta} \right) \frac{dT}{T} + \sum_r' \left\{ \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) + \frac{e^\sigma (x_1^\alpha x_r^\beta - x_r^\alpha x_1^\beta)}{e^\beta x_1^\alpha} \right\} RTD \log p_r^\alpha. \quad (7, 14)$$

\* The quantities which I have denoted by  $h^\beta$ ,  $e^\beta$ ,  $h^\sigma$ ,  $e^\sigma$  would be more reasonably denoted by  $h^{\alpha\beta}$ ,  $e^{\alpha\beta}$ ,  $h^{\alpha\sigma}$ ,  $e^{\alpha\sigma}$ , or better still by  $h^{\alpha \rightarrow \beta}$ ,  $e^{\alpha \rightarrow \beta}$ ,  $h^{\alpha \rightarrow \sigma}$ ,  $e^{\alpha \rightarrow \sigma}$ . My choice of the shorter symbols has been made to facilitate printing.

Either of formulæ (7, 11) and (7, 14) may be regarded as the fundamental formula of the present treatment.

If both the phases  $\alpha$  and  $\beta$  are liquid it can happen that  $e^\beta$  is zero. The equilibrium between  $\alpha$  and  $\beta$  is then independent of  $P$ , and so we are obliged to retain  $P$  as an independent variable; the coefficient of  $P$  in (7, 3) vanishes, and so we cannot eliminate  $P$  between (7, 3) and (7, 4). However, the vanishing of  $e^\beta$  implies that the tightness of packing of the molecules is the same in phases  $\alpha$  and  $\beta$  (*i.e.* equal partial molar volumes in the two phases) and one may then with some confidence expect the same tightness of packing in  $\sigma$ . In this case,  $e^\sigma$  is also zero, wherever one places the plane  $BB'$ ; thus the coefficient of  $dP$  in (7, 4) is zero. If then we eliminate  $D\mu^\alpha$  from (7, 4) by means of (6, 5), we now obtain in place of (7, 11) the simpler result

$$-d\gamma = h^\sigma \frac{dT}{T} + \Sigma_r' \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) D\mu_r^\alpha, \quad (7, 11a)$$

and correspondingly, in place of (7, 14),

$$-d\gamma = h^\sigma \frac{dT}{T} + \Sigma_r' \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) RTD \log p_r^\alpha. \quad (7, 14a)$$

### 8. Invariance of Fundamental Formula.

Although the quantities  $\Gamma_r$ ,  $h^\sigma$  and  $e^\sigma$  have simple physical meanings, their values will depend on the positions assigned to the planes  $AA'$  and  $BB'$  which bound the surface layer. It can be shown, however, that formula (7, 11) remains invariant when either of the planes is shifted.

Let us first consider a shift of the plane  $AA'$  a distance  $\delta\tau$  away from  $BB'$ . Then  $\Gamma_r$  becomes increased by the number of moles in a cylinder of  $\alpha$  of height  $\delta\tau$ , of unit cross-section, and consequently of volume  $\delta\tau$ . If, therefore,  $C^\alpha$  denotes the total number of moles of any kind per unit volume in  $\alpha$ , then  $\Gamma_r$  becomes increased by  $x_r^\alpha C^\alpha \delta\tau$ . Similarly,  $\Gamma_1$  becomes increased to  $x_1^\alpha C^\alpha \delta\tau$ . Hence  $(\Gamma_r - \Gamma_1 x_r^\alpha / x_1^\alpha)$  remains invariant. Furthermore, it is clear from their definitions that  $h^\sigma$  and  $e^\sigma$  remain invariant when the plane  $AA'$  is shifted. Hence formula (7, 11) is invariant with respect to a shift of the plane  $AA'$ .

Let us now consider a shift of the plane  $BB'$  a distance  $\delta\tau$  away from  $AA'$ . In this case, if  $C^\beta$  denotes the total number of moles of any kind per unit volume in the phase  $\beta$ ,  $\Gamma_r$  becomes increased by  $x_r^\beta C^\beta \delta\tau$ ; at the same time  $h^\sigma$  becomes increased by  $h^\beta C^\beta \delta\tau$  and  $e^\sigma$  becomes increased by  $e^\beta C^\beta \delta\tau$ . If we substitute into (7, 11) it becomes immediately evident that the coefficients of  $dT$  and of each  $D\mu_r^\alpha$  all remain invariant.

We see then that the coefficients of  $dT$  and each  $D\mu_r^\alpha$  in (7, 11) or (7, 14) have values independent of the positions assigned to  $AA'$  and  $BB'$ .

### 9. Temperature Coefficient of Interfacial Tension.

If we consider variations of temperature at constant composition of the (liquid) phase  $\alpha$ , the pressure and the composition of the (gaseous or liquid) phase  $\beta$  being adjusted so as to maintain equilibrium, then all the  $D\mu_r^\alpha$  are zero. Formula (7, 11) or (7, 14) now reduces to

$$T \frac{d\gamma}{dT} = h^\sigma - \frac{e^\sigma h^\beta}{e^\beta}. \quad (9, 1)$$

A formula equivalent to (9, 1) has been obtained by Verschaffelt<sup>4</sup> for the special case of a simple liquid-vapour interface. For the general case of several components this formula is, so far as I know, new.

It has been verified in the previous section that the right side of (1) is invariant with respect to displacement of the plane BB', while each term is separately invariant with respect to displacement of the plane AA'. If the plane BB' can be so placed that  $e^\sigma$  vanishes, then (9, 1) reduces to

$$T \frac{dy}{dT} = h^\sigma, \quad (9, 2)$$

but the physical significance of this arbitrary choice of the plane BB' is far from obvious. Only in the special case referred to at the end of section 7 is formula (9, 2) valid wherever BB' be placed.

### 10. Dependence of Superficial Tension on Composition.

For variations of composition at constant temperature formula (7, 14) reduces to

$$-dy = \sum_r' \left\{ \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) + \frac{e^\sigma (x_1^\alpha x_r^\beta - x_r^\alpha x_1^\beta)}{e^\beta x_1^\alpha} \right\} RTD \log p_r. \quad (10, 1)$$

In the simple case of only two components this reduces further to

$$-dy = \left\{ \left( \Gamma_2 - \frac{x_2^\alpha \Gamma_1}{x_1^\alpha} \right) + \frac{e^\sigma (x_2^\beta - x_2^\alpha)}{e^\beta x_1^\alpha} \right\} RTD \log p_2. \quad (10, 2)$$

It has been verified in section 8 that the right side of (10, 1) is invariant with respect to displacements of the planes AA' and BB'. If the plane BB' can be so placed that  $e^\sigma$  vanishes, then (10, 1) reduces to

$$-dy = \sum_r' \left( \Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha} \right) RTD \log p_r. \quad (10, 3)$$

If, moreover, the plane AA' can be so placed that  $\Gamma_1$  vanishes, then (10, 3) reduces further to

$$-dy = \sum_r' \Gamma_r RTD \log p_r. \quad (10, 4)$$

However, I believe that these algebraic contractions are achieved only at the cost of physical clarity (*Anschaulichkeit*) with respect to the meaning of the  $\Gamma_r$ 's. Only in the special case referred to at the end of section 7 is formula (10, 3) valid wherever BB' be placed.

### 11. Inert Components.

It is conceivable that certain components present in the phase  $\beta$  have a uniform concentration throughout  $\beta$  down to a certain plane where they fall abruptly to zero and remain zero across it and inside  $\alpha$ . It will then be natural to choose this plane as BB' the boundary between  $\beta$  and  $\sigma$ . These components may be called inert components, and will be denoted by the subscript  $i$ ; the remaining components will be denoted by the subscript  $a$ . The number of components of the two classes will also be denoted by  $i$  and by  $a$  respectively. By using this notation formula (7, 4) becomes

$$-dy = (s^\sigma - \Sigma_a \Gamma_a s_a^\alpha) dT - (\tau - \Sigma_a \Gamma_a \tau_a^\alpha) dP + \Sigma_a \Gamma_a D \mu_a^\alpha, \quad (11, 1)$$

since all the  $\Gamma_i$ 's are by supposition zero. Similarly, the Gibbs-Duhem relation (6, 5) becomes

$$\Sigma_a x_a^\alpha D\mu_a^\alpha = 0, \quad (11, 2)$$

since by supposition all the  $x_i^\alpha$ 's are zero. By means of (11, 2) we can eliminate one of the  $D\mu_a^\alpha$ 's, say  $D\mu_1^\alpha$  from (11, 1). We obtain

$$-d\gamma = (s^\sigma - \Sigma_a \Gamma_a s_a^\alpha) dT - (\tau - \Sigma_a \Gamma_a v_a^\alpha) dP + \Sigma_a' \left( \Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha} \right) D\mu_a, \quad (11, 3)$$

or in terms of  $h^\sigma$  and  $e^\sigma$  defined in section 7,

$$-d\gamma = h^\sigma \frac{dT}{T} - e^\sigma dP + \Sigma_a' \left( \Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha} \right) D\mu_a. \quad (11, 4)$$

The number of differentials on the right of (11, 4) is  $(a + 1)$ , whereas the number of degrees of freedom of the whole system is  $(a + i)$ . Hence, as long as there is at least one inert component so that  $i \geq 1$ , the differentials on the right of (11, 4) are all independent. The physical explanation is that (11, 4) is a relation involving only properties of the phases  $\alpha$  and of the interfaces  $\sigma$ ; no properties of the phase  $\beta$  occur explicitly in (11, 4). The inert components present only in  $\beta$  are therefore available for adjusting the pressure  $P$  on the phase  $\alpha$  without any need of altering its temperature or its composition. It is easily verified that each term on the right of (11, 4) is invariant with respect to displacements of the plane  $AA'$ . In the present case the plane  $BB'$  is naturally fixed.

The treatment just described is particularly applicable to the interface between a liquid solution and the gaseous phase above it, when some of the gaseous constituents can be treated as inert components. The applications of formula (11, 4) are obvious. For example, we have for the temperature coefficient of  $\gamma$  at constant pressure and composition of the phase  $\alpha$

$$-\left(\frac{\partial \gamma}{\partial T}\right)_{P, x_a} = \frac{h^\sigma}{T}. \quad (11, 5)$$

Similarly, for the pressure coefficient of  $\gamma$  at constant temperature and composition of the phase  $\alpha$ ,

$$\left(\frac{\partial \gamma}{\partial P}\right)_{T, x_a} = e^\sigma. \quad (11, 6)$$

Finally, for variations of composition at constant temperature and pressure, we have

$$-d\gamma = \Sigma_a' \left( \Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha} \right) D\mu_a = \Sigma_a' \left( \Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha} \right) RT D \log p_a^\alpha. \quad (11, 7)$$

The formulæ of this section are mostly familiar,\* but the restrictive conditions for their validity seem to be less widely recognised.

## 12. Relation to Gibbs' Formulæ.

We have already verified that our formulæ remain invariant when either or both the planes  $AA'$  and  $BB'$  are shifted, as long as the inhomogeneous layer is contained between  $AA'$  and  $BB'$ . Let us now

\* The expression  $(\Gamma_a - \Gamma_1 x_a^\alpha / x_1^\alpha)$  occurring in (11, 3), (11, 4) and (11, 7) is equivalent to Guggenheim and Adam's  $\Gamma_a^{(1)}$  or to Gibbs'  $\Gamma_{a(1)}$ .

consider what happens if we move one of these planes towards the other until part of the inhomogeneous layer is on the outer side of the former plane. It is quite easy to see that all our formulæ can be made to remain unaltered, provided we alter our definitions of the symbols. We must now define  $F^\alpha$  not as the free energy of the actual phase  $\alpha$  up to the plane  $AA'$ , but as equal to the free energy of a fictitious phase  $\alpha$  supposed to remain homogeneous right up to  $AA'$ . Similarly, we define  $F^\beta$  not as the free energy of the actual phase  $\beta$  down to the plane  $BB'$ , but as equal to the free energy of a fictitious phase  $\beta$  supposed to remain homogeneous right down to  $BB'$ . Finally, we define  $F^\sigma$  as the excess of the free energy  $F$  of the whole system over and above  $F^\alpha + F^\beta$  as just defined. We give analogous definitions to  $S^\alpha, S^\beta, S^\sigma; V^\alpha, V^\beta, V^\sigma; n_r^\alpha, n_r^\beta, n_r^\sigma$ .

As long as the planes  $AA'$  and  $BB'$  enclose the inhomogeneous layer, the new definitions of the thermodynamic functions relating to the surface are exactly equivalent to the ones used initially. The latter are certainly easier to visualise and are in this respect preferable. The only advantage of the former is that they allow us to place the two planes  $AA'$  and  $BB'$  as near to each other as we please, regardless of the structure of the surface layer, without affecting the validity of our formulæ. In particular we may, if we choose, make the planes  $AA'$  and  $BB'$  coincide. If we do this  $V^\sigma$  and  $\tau$  become zero, some of the  $n_r^\sigma$ 's and  $\Gamma_r^\sigma$ 's may become negative and our formulæ reduce to those of Gibbs.

We may therefore describe Gibbs' formulæ as formally included in those of the present treatment. However, I believe that the mathematical elegance of Gibbs' formulæ is attained only at the cost of a certain obscurity in the physical significance of the symbols used. In the formulæ of the present treatment all the symbols have a simple physical definition with respect to an arbitrary pair of parallel planes enclosing the inhomogeneous layer.

In conclusion, it is interesting to note that Gibbs himself realised the existence of alternative formulations and recognised the possibility that the formulation, which he himself developed, might for certain purposes be less convenient than some alternative formulation.<sup>5</sup> I therefore hope the reader will regard the treatment, which I have described, as an attempt to follow the guidance of Gibbs without, however, following blindly.

I am indebted to Professor N. K. Adam, F.R.S., for his helpful and constructive criticism.

## Part II. Curved Interfaces.

### 1. Introduction.

The object of Part II of this paper is to study the following question. What conditions are sufficient to justify the application to curved interfaces of the formulæ already derived for plane interfaces? As answer to this question we shall find that the formulæ strictly derived for plane interfaces may be applied to curved interfaces with an accuracy adequate for experimental purposes, provided that *the thickness of the inhomogeneous layer is small compared with its radii of curvature.*

<sup>5</sup> Gibbs, *loc. cit.*<sup>1</sup> Footnote on p. 267.

I shall first give a direct and simple derivation of this condition. We shall then see that this condition is in fact assumed implicitly by every experimenter when he measures a superficial tension and that when it is not satisfied the superficial tension and related properties of the interface become ill-defined. In conclusion, I shall discuss briefly Gibbs' treatment of the same subject.

## 2. Interfacial Tension of Curved Interface.

For the sake of simplicity let us first consider a system consisting of two homogeneous bulk phases  $\alpha$  and  $\beta$  connected by a surface layer  $\sigma$

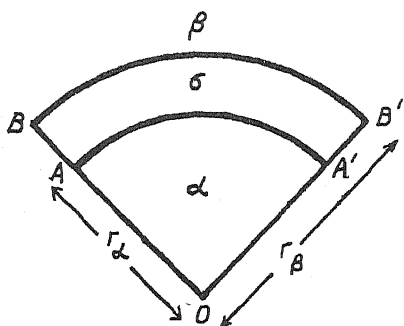


FIG. 2.

having the form of a circular cylindrical shell. Fig. 2 shows a cross-section of the phases  $\alpha$  and  $\beta$  separated by the surface layer  $\sigma$ , bounded by the circular cylinders  $AA'$  and  $BB'$  with common axis  $O$ . There is complete homogeneity in the direction normal to the diagram. The properties of the surface layer  $\sigma$  are supposed identical at all points the same distance from the axis through  $O$ . Throughout the phase  $\alpha$  and extending up to  $AA'$  there is a uniform pressure  $P^\alpha$ ; throughout

the phase  $\beta$ , and extending down to  $BB'$ , there is a uniform pressure  $P^\beta$ . Between  $AA'$  and  $BB'$  the pressure  $P_r$  parallel to the radii of the cylinders  $AA'$  and  $BB'$  varies continuously, but not necessarily monotonically, from the value  $P^\alpha$  to the value  $P^\beta$ .

In the previous discussion of plane surfaces it was pointed out that the geometrical planes  $AA'$  and  $BB'$  could be placed an arbitrary distance apart, provided that the inhomogeneous layer was contained between them. For the present discussion of curved surfaces it is on the contrary essential that the circular cylindrical surfaces  $AA'$  and  $BB'$  should be placed as near together as is consistent with the condition that the inhomogeneous layer be contained between them. According to this condition we may usually expect the distance  $AB$  to be about  $10^{-7}$  or  $10^{-6}$  cm. I shall denote by  $r$  distances measured radially from  $O$ , and in particular by  $r_\alpha$  and  $r_\beta$ , the distances  $OA$  and  $OB$  respectively.

Whereas the force per unit area across any element of surface inside either homogeneous phase is independent of the orientation of the element (Pascal's Law), this is not the case in the inhomogeneous layer  $\sigma$ . It is convenient to denote the force per unit area in the direction parallel to the surfaces  $AA'$  and  $BB'$  by  $P_r - Q$ . Both  $P_r$  and  $Q$  are functions of  $r$ .  $Q$  is zero at  $r = r_\alpha$  and at  $r = r_\beta$ , but at least somewhere between  $Q$  is greater than zero. [It is conceivable that  $Q$  might be negative somewhere between  $r = r_\alpha$  and  $r = r_\beta$ , but its average value in this range is unquestionably positive.]

According to elementary statics the mechanical equilibrium of the matter enclosed by  $AA'B'B$  requires that for all values of  $r$

$$d(P_r) = (P_r - Q)dr, \quad (2, 1)$$

or

$$dP_r = -Qdr/r. \quad (2, 2)$$

If we integrate (2, 2) from  $r_\beta$  to  $r_\alpha$  we obtain

$$P^\alpha - P^\beta = \int_{r_\alpha}^{r_\beta} \frac{Q}{r} dr. \quad (2, 3)$$

We now define quantities  $\bar{r}$ ,  $\gamma$ ,  $\gamma'$  by

$$2\bar{r} = r_\alpha + r_\beta, \quad (2, 4)$$

$$\gamma = \int_{r_\alpha}^{r_\beta} Q dr, \quad (2, 5)$$

$$\gamma' = \bar{r} \int_{r_\alpha}^{r_\beta} \frac{Q}{r} dr. \quad (2, 6)$$

According to (2, 6) we can rewrite (2, 3) in the form

$$P^\alpha - P^\beta = \gamma' / \bar{r}. \quad (2, 7)$$

If now  $(r_\beta - r_\alpha) \ll r_\alpha$ , so that we may ignore the distinction between  $r_\alpha$ ,  $r_\beta$ ,  $\bar{r}$ , then we may also ignore the distinction between  $\gamma$  and  $\gamma'$ , and instead of (2, 7) we may write

$$P^\alpha - P^\beta = \gamma / \bar{r}. \quad (2, 8)$$

Under these conditions either  $\gamma$  or  $\gamma'$  may be regarded as the interfacial tension.

For the sake of simplicity we have confined our attention to an interface in the form of a circular cylinder. For a spherical interface we should have found by analogous reasoning, instead of (2, 8),

$$P^\alpha - P^\beta = 2\gamma / \bar{r}. \quad (2, 9)$$

For an interface of arbitrary shape the geometry is somewhat more complicated and the general formula obtained is

$$P^\alpha - P^\beta = \gamma \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right), \quad (2, 10)$$

where  $\rho_1$ ,  $\rho_2$  are the principal radii of curvature of the interface.

Formula (2, 10) is well known and, moreover, forms the basis of the experimental determinations of superficial tension. The quantities  $\rho_1$ ,  $\rho_2$  and  $P^\alpha - P^\beta$  are measured, and then  $\gamma$  is calculated according to (2, 10). The best known method, that of the capillary rise, has already been discussed elsewhere<sup>6</sup> in relation to formula (2, 10). The point which I wish to emphasise is that, since formula (2, 10), like formulae (2, 8) and (2, 9), implies ignoring the difference between lengths such as  $r_\alpha$ ,  $r_\beta$ , it follows that *the very measurement of interfacial tension implies that the thickness of the surface layer be small compared with its radii of curvature.*

### 3 Discussion of Pressure Difference.

Although the pressure difference  $P^\alpha - P^\beta$  is fundamental in the measurement of  $\gamma$ , and so also one may say in the definition of  $\gamma$ , I shall show that this pressure difference is in certain other respects insignificant for the properties of the interface. I shall use the symbol  $\tau$  to denote the thickness of the surface layer, hitherto denoted by  $r_\beta - r_\alpha$ . Let us consider a numerical example. We will suppose that  $\tau = 10^{-7}$  cm. and that  $\gamma = 50$  dynes/cm. Since the treatment requires that both principal radii of curvature satisfy the inequality  $\rho \gg \tau$ , if we aim at an accuracy

<sup>6</sup> Guggenheim, *Modern Thermodynamics*, p. 169 (Methuen 1933).



of the order 1 %, then  $\rho$  must not be less than 100  $\tau$  or  $10^{-5}$  cm. According to formula (2, 10) we conclude that  $P^\alpha - P^\beta$  is at most  $10^7$  dynes/cm.<sup>2</sup> or 10 atmospheres. I have chosen a very unfavourable case and usually  $P^\alpha - P^\beta$  will be only a small fraction of an atmosphere. Thus the product  $(P^\alpha - P^\beta)$  cannot be greater than 1 dyne/cm. or 1 erg/cm.<sup>2</sup>.

According to formula (2, 2) of Part I the total work done on a plane surface layer when its volume and area are altered is

$$- PdV^\sigma + \gamma dA. \quad (3, 1)$$

We could apply this formula also to a curved surface were it not for an ambiguity in the meaning of  $P$ . Since, however, we have verified that  $(P^\alpha - P^\beta)\tau$  or  $(P^\alpha - P^\beta)V^\sigma/A$  is at most 2 % of  $\gamma$  and usually much smaller, we may safely ignore this ambiguity. Thus (3, 1) is sufficiently accurate if  $P$  denotes  $P^\alpha$  or  $P^\beta$  or any intermediate pressure. In virtue of the validity of (3, 1) for curved as well as plane interfaces, any of the formulæ of Part I are equally valid to the same degree of accuracy.

#### 4. Dependence of Interfacial Tension on Curvature.

Let us now turn to the question of how the interfacial tension depends on the curvatures. We shall see that when the question is precisely defined it answers itself. In asking the question it is not sufficient to state that we vary the curvatures; we require also to state what we keep constant. For the question to be useful it should apply to the actual conditions of the experimental measurement of interfacial tension. For definiteness let us consider the capillary rise method. The values of the temperature  $T$  and the potentials  $\mu_r$  are uniform throughout the system,\* and so, whatever be the size and shape of the capillary, these variables have the same values at the curved surface where the surface tension is measured, as in the bulk phases. Hence to be useful the question should be worded: how does  $\gamma$  depend on  $\rho_1, \rho_2$  for given values of  $T$  and the  $\mu$ 's. According to equation (5, 1) of Part I the variation of  $\gamma$  under these restrictions is given by

$$d\gamma = \tau dP. \quad (4, 1)$$

In its present application the ambiguity in the exact meaning of  $P$  does not matter, since we have already verified that  $P^\alpha - P^\beta$  is negligible. If now we consider a curved interface, say in a capillary, in equilibrium with a plane interface and we integrate (4, 1) from the pressure at the plane surface to the pressure at the curved interface (either side of it) we again find that the integral of the right side is always negligible. Consequently  $\gamma$  has effectively the same value for the curved surface as for the plane surface with which it is in equilibrium. This is a statement of a principle usually assumed whenever an interfacial tension is measured. It is experimentally verified by the fact that within the experimental accuracy the same value is found for the interfacial tension when capillaries of different size are used, but this verification can be realised only for capillaries with diameters considerably greater than the lower limit  $10^{-5}$  cm., allowed by the theory.

\* For this statement to be true it is necessary that a gravitational term  $M_r g h$  be included in  $\mu_r$ , where  $M_r$  denotes molar mass,  $g$  gravitational acceleration and  $h$  height. But it is physically obvious that the interfacial tension cannot depend on the height except through the pressure and composition. Such gravitational terms may therefore safely be omitted from the  $d\mu_r$ 's in the formulæ relating  $d\gamma$  to the  $d\mu_r$ 's.

### 5. Gibbs' Treatment.

The problem, which I have discussed, is treated by Gibbs<sup>7</sup> in a manner which appears to be quite different and more rigid. I have found Gibbs' treatment difficult and the more carefully I have studied it the more obscure it appears to me. The essence of Gibbs' treatment is that he replaces the term

$$\gamma dA \quad . \quad . \quad . \quad . \quad . \quad (5, 1)$$

for a plane interface by terms of the form

$$\gamma dA + C_1 d\left(\frac{I}{\rho_1}\right) + C_2 d\left(\frac{I}{\rho_0}\right), \quad (5, 2)$$

and assumes implicitly that, provided the radii of curvature are not too small, we may assign to  $C_1$  and  $C_2$  the values appropriate to a plane surface. It is then obvious from symmetry that  $C_1 = C_2$ , and so (5, 2) can be written in the simpler form

$$\gamma dA + Cd\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right), \quad (5, 3)$$

where  $C$  is independent of  $\rho_1, \rho_2$ . So far so good. Gibbs then sets out to prove that his geometrical surface can be so placed that  $C$  vanishes. The reasoning adduced is far from simple, and Gibbs' meaning is not even always clear. I am convinced that Gibbs was himself aware of the difficulty of being precise in this particular piece of reasoning. On page 226 he discusses the variation of a plane interface by bending it and uses the sentence "also at and about the surface let the state of the matter *so far as possible be the same* as at and about the plane surface in the initial state of the system." The words which I have written in italics are, I venture to say, in their vagueness unlike Gibbs' usual style. The whole treatment of Gibbs, as well as that of the present paper, postulates complete equilibrium throughout the whole system. It is therefore impossible to conceive of a variation of an interface apart from a variation in at least one of the bulk phases. It is clear that Gibbs realised this difficulty and tried to overcome it by flexible wording.

On the following page Gibbs claims to show that the position required for his geometrical surface to make  $C$  vanish will be either inside the non-homogeneous layer or at most at a distance from it comparable to the thickness of the layer. He here uses the words "on account of the thinness of the non-homogeneous film," and I feel convinced that this *thinness* is an essential assumption common to Gibbs' treatment and that outlined above. If then, as I believe, the assumption  $\tau \ll r_\alpha$  is essential, it seems to me preferable to introduce it at the outset and so considerably simplify the whole argument.

### Summary.

### Part I.—

Following Verschaffelt the thermodynamic properties of a plane interface are derived by treating the interface as having a finite thickness. Formulæ are derived for the dependence of the interfacial tension on the temperature and the composition of one of the two bounding phases; the pressure, not being an independent variable, is eliminated. It is shown that the formulæ are invariant with respect to the thickness arbitrarily assigned to the interfacial layer. The treatment is correlated with that of Gibbs.

<sup>7</sup> Gibbs, *Collected Works*, vol. 1, pp. 225-228.

## Part II.—

It is shown that the formulæ derived in Part I for plane interfaces may safely be applied to curved interfaces provided that the thickness of the inhomogeneous layer is negligibly small compared with its radius of curvature, a condition usually fulfilled in practice. When this condition is not fulfilled, the formulæ cease to be applicable and at the same time the normal methods of measuring interfacial tension break down and the very meaning of interfacial tension becomes ill-defined.

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## CONTACT ANGLES OF "BUILT-UP" MULTILAYERS.

BY J. J. BIKERMAN.

*Received 13th November, 1939.*

### 1. Introduction.

The formation of "built-up" X, Y, or Z multilayers was recently<sup>1</sup> correlated to the wettability of the solid surfaces concerned; when this increased the transition  $X \rightarrow Y \rightarrow Z$  took place. As a measure of wettability the angle  $\alpha$  of sliding of a water drop on the multilayer was used. It was shown that in a first approximation the product  $W \tan \alpha$ ,  $W$  being the weight of the sliding drop, was a constant for a given multilayer and could be taken as a measure of its hydrophilic character.

In the present work the wettability of a surface is determined by measuring the wetting angles  $\theta$  formed by the solid, a water drop on it, and air. When  $\theta$  was over  $94^\circ$  X films were deposited. Y films were observed when  $\theta$  was greater than  $80^\circ$  and less than  $92^\circ$ . Smaller  $\theta$  values favoured Z depositions.

### 2. Experimental Technique.

#### (a) Water-line Corrosion of Multilayers.

For measuring the contact angle  $\theta$  a new method was devised which is especially convenient for multilayers but may, with slight modification, also be adapted to determination of contact angles on other solid surfaces (see the last paragraph of 2 (b)).

TABLE I.

*Time in mins.     $\theta$  in deg.*

0	90
5	76
10	72
15	51
20	42
30	42

If a water drop be put on a multilayer deposited on a chromium-plated slide it changes form within a few seconds. A fraction of a second after it has touched the surface the contact angle viewed with a projection microscope may be, say,  $90^\circ$ , but it diminishes rapidly. A typical example is given in Table I referring to a film of 38 monolayers of barium stearate.

The reason, or one of the reasons, for this decrease of  $\theta$  was apparent when the drop was thrown off the slide. It left on the multilayer a coloured trace in the form of a narrow ring. As the thickness of a multilayer can be

<sup>1</sup> J. J. Bikerman, *Proc. Roy. Soc. A*, 1939, **170**, 130.

determined from its interference colour it was possible to estimate the depth of the circular "groove"; it turned out to be about 3 molecules. The width of the groove varied with the substance of the multilayer; it was less than 0.001 cm. for calcium stearate films, about 0.002 cm. for barium stearate, etc.

Obviously it was a case of "water-line corrosion."<sup>2</sup> Soap films which are practically insoluble in water are corroded along the water-film-air boundary because soaps lower the surface tension of water and are drawn into the water-air interface. The reduction of the surface tension thus produced caused a reduction of the contact angle in agreement with the well-known equation

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}, \quad . \quad . \quad . \quad . \quad (1)$$

where  $\gamma_{sg}$ ,  $\gamma_{sl}$ , and  $\gamma_{lg}$  are the interfacial tensions between solid and gas, solid and liquid, and liquid and gas respectively. A lowering of  $\gamma_{lg}$  causes a lowering of  $\theta$ . The validity of equation (1) is discussed in 4 (c).

Water droplets on multilayers having large contact angles (e.g. octadecyl acetate) usually evaporated very slowly, whilst those on the multilayers of hydrophilic octadecyl amine disappeared within a few minutes. Presumably water penetrates into hydrophilic films and spreads over the whole area of the multilayer, thus increasing the area from which evaporation takes place.

Droplets on mixed multilayers (for instance of 6 molecules of octadecyl amine + 2 molecules of calcium stearate + 6 amine + 2 stearate + 6 amine + 2 stearate + 6 amine + 4 stearate) produced no rings.

### (b) Computation of Contact Angles.

The diameter  $\Delta$  of the circular groove left by a drop was found to agree with the initial value  $\theta$  of the wetting angle and not with the value observed shortly before throwing off the drop.

The general relation between  $\Delta$  and  $\theta$  is difficult to calculate, as the fundamental equation of capillarity

$$-h\rho g + \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \text{const.}, \quad . \quad . \quad . \quad (2)$$

leads at once to elliptic integrals;  $h$  is the vertical distance of a point on the drop surface from the summit of the drop,  $\rho$  the density of water minus the density of air,  $g$  the acceleration due to gravity,  $\gamma$  the surface tension, and  $R_1$  and  $R_2$  the principal radii of curvature. If, however, the drop may be assumed to be a spherical segment, then

$$\Delta_0 = 2R \sin \theta, \quad . \quad . \quad . \quad . \quad (3)$$

where  $R$  denotes the radius of the sphere (or the radius of the curvature of the drop);  $\Delta_0$  is  $\Delta$  for drops having a spherical curvature. As it is more difficult to determine the curvature of a drop than its volume  $v$ ,  $R$  may be expressed in terms of  $v$ . The volume of a spherical segment is

$$v = \pi R^3 \left( \frac{2}{3} - \cos \theta + \frac{1}{3} \cos^3 \theta \right). \quad . \quad . \quad . \quad (4)$$

From (3) and (4) the relation

$$\frac{\Delta_0^3}{v} = \frac{24 \sin^3 \theta}{\pi (2 - 3 \cos \theta + \cos^3 \theta)} \quad . \quad . \quad . \quad (5)$$

is obtained. The numerical values of the right hand function were calculated for several values of  $\theta$ , and the table obtained was used for evaluation of  $\theta$  from  $\Delta_0$  and  $v$ .

<sup>2</sup> See e.g. U. R. Evans, *Metallic Corrosion*, 1937, pp. 178, 296; M. Volmer and Mahnert, *Z. physik. Chemie*, 1925, 115, 239.

It is obvious, and also follows from (2), that the deviation of the drop shape from that of a spherical segment diminishes when the volume  $v$  is reduced. To apply (5), the ratio  $\Delta^3/v$  was therefore measured for several drops of various sizes and then extrapolated to  $v = 0$ .

For the case of  $\theta = 90^\circ$  the graphical extrapolation to  $v = 0$  can be checked by calculation. Equations (3) and (4) neglect gravitation altogether. Gravitation flattens the drops which, in the second approximation, may be considered to be (at  $\theta = 90^\circ$ ) halves of ellipsoids of revolution; introducing their radii of curvature ( $a$  and  $b$  being the half-axes) (2) becomes

$$-h\rho g + \gamma\left(\frac{1}{a} + \frac{a}{b^2}\right) = \frac{2\gamma b}{a^2}. \quad (6)$$

On the other hand,

$$v = \frac{2}{3}\pi a^2 b. \quad (7)$$

Setting  $h = b$  and  $\Delta/2 = a$  we obtain at small values of  $v$  and after introducing  $v^2 = a^2 b = 3v/2\pi$

$$\Delta - 2\gamma = \frac{\rho g v^2}{6\gamma - \rho g v^2}, \quad (8)$$

and

$$\frac{\Delta^3}{v} = \frac{6}{\pi} \left( 2 + \frac{3\rho g v^2}{6\gamma - \rho g v^2} \right). \quad (9)$$

In deducing (9) it is assumed that the contact angle is independent of the size of the drop. As the experimental curves of the function  $\Delta^3/v = f(v)$  were quite similar to the theoretical curve this assumption appears to be justified.<sup>3</sup>

The method outlined above can be applied to other solid surfaces. If the liquid contains non-volatile matter,  $\Delta$  is the diameter of the circle covered by residue. If the liquid evaporates without leaving marks it may be sprayed over with ignited talc which slides down to the circumference of the drop.

### (c) Precision of the Results.

The drops were driven out from a calibrated micro-syringe<sup>4</sup> and the volume  $v$  of the drop was read directly; the error involved, except for the very small drops,<sup>5</sup> was negligible. The diameter  $\Delta$  of the corrosion ring was measured at a magnification of 20 with a scale and the precision depended chiefly on the degree of deviation of the ring from the truly circular shape. If the drops were not too small two apparently identical drops gave on good surfaces values of  $\Delta^3/v$ , agreeing within 1%, and as the error of extrapolation is less than 0.5%, the true value of  $\Delta_0^3/v$  is known to 1.5%, corresponding to an error of  $\pm 15'$  in the values of contact angles.

The differences between the contact angles on two different slides coated with supposedly identical multilayers were much larger and often exceeded  $2^\circ$ .

The values of  $\Delta$  used for calculations were those of external diameters of the ring marks. If the internal diameters were taken all the values of  $\theta$  would be raised by 1% or more; indeed they would become greater than the contact angles observed with a projection microscope directly after deposition of drops.

<sup>3</sup> See F. E. Bartell and Merrill, *J. phys. Chem.*, 1932, **36**, 1178.

<sup>4</sup> In this case the difficulties which Bartell and Hatch (*ibid.*, 1935, **39**, 11) encountered when placing drops on solids were insignificant.

<sup>5</sup> The range of volumes used was 0.001 to 0.020 c.c.

### 3. Results.

A selection of the results obtained is given in Table II. The first column indicates the number, the type, and the composition of the "built-up" monolayers on chromium plated slides. The second and third

TABLE II.

Multilayer.	pH.	Buffer.	$\Delta_0^3/v$ .	$\theta$ .
40 X octadecyl acetate . .	7.4	Phosphate .	2.79	101.2°
38 X calcium stearate . .	9.1	Borate .	3.12	97.5°
38 (X + Y) calcium stearate .	—	Borate .	3.56	92.6°
38 Y barium stearate . .	7.4	Phosphate .	3.87	89.5°
38 Y barium stearate . .	7.4	Phosphate .	3.93	89.1°
38 Y barium stearate . .	7.4	Phosphate .	4.00	88.2°
44 Y barium palmitate . .	7.4	Phosphate .	4.30	85.5°
38 Y octadecyl amine . .	7.4	Phosphate .	5	80°

columns refer to the underlying solution from the surface of which the monolayers were taken up. The meaning of  $\Delta_0^3/v$  and  $\theta$  is explained in 2 (b).

The multilayer described as 38 (X + Y) calcium stearate was a mixture of X and Y deposited films (see the previous paper<sup>1</sup>); the slide was dipped 22 times, and the area of film consumed corresponded to a deposition of 38 monolayers. The three values for barium stearate illustrate the differences between multilayers taken off the surfaces of apparently identical solutions.

### 4. Discussion.

#### (a) Wetting Angle and Deposition of Multilayers.

Table III contains the rule based on the explanation recently advanced<sup>1</sup> for the three types of deposition of multilayers on solid slides.

TABLE III.

	Multilayers.		
	X.	Y.	Z.
A monolayer is taken up in the course of	dipping only	both dipping and withdrawal	withdrawal only
if the contact angle (measured in the liquid) is	always greater than 90°	over 90° at dipping and below 90° at withdrawal	always below 90°

It deals with receding and advancing contact angles, which may be compared with the equilibrium contact angles listed in Table II. It is seen that Y layers are only deposited when the equilibrium wetting angle is near 90°, so that the receding angle (*i.e.* during withdrawal) may easily become < 90° and the advancing angle (*i.e.* at dipping) > 90°. At the speeds used in the multilayer technique the range of  $\theta$  values giving Y

layers extends from about  $80^\circ$ \* to  $92^\circ$ . It is asymmetrical about  $90^\circ$  presumably because, in agreement with Blodgett's advice,<sup>6</sup> the dipping is carried out swiftly (whereby the difference between the equilibrium angle  $\theta$  and the advancing angle is large) and the withdrawal slowly (thus diminishing the difference between  $\theta$  and the receding angle).

### (b) Wetting Angles and Chemical Composition.

Langmuir<sup>7</sup> considers the wetting angles to be determined by the most external radical of the molecule of the solid, *i.e.* for substances treated here, by the  $\text{CH}_3$  group. As the wetting angles differ from substance to substance, it is suggested that the outer layer of a "built-up" film contains some "overturned" molecules so that some hydrophilic groups also are exposed. Since it was shown in the previous paper<sup>1</sup> that the multilayers usually had no specific structure the hypothesis of Langmuir cannot be accepted. Evidently the wetting angle of a substance is related to its whole chemical structure in the same manner as are its other physical properties.

### (c) Wetting Angles and Interfacial Tensions.

The following observation casts some doubt upon the general validity of the usual theory of contact angles. A water drop placed on a hydrophobic surface<sup>†</sup> forms a wetting angle of, say,  $100^\circ$ . If a drop of ether hanging on a glass rod is brought near, the shape of the water drop does not change although, with a projection microscope, ether vapours can be seen descending onto the water surface.

According to (1) constant  $\theta$  involves constant  $(\gamma_{\text{SG}} - \gamma_{\text{SL}})/\gamma_{\text{LG}}$ . Since diffusion of ether through the drop to the solid-liquid interface would take some time,  $\gamma_{\text{SL}}$  may be assumed to be unaffected by ether. Then the improbable result follows that the alterations of  $\gamma_{\text{SG}}$  and  $\gamma_{\text{LG}}$  just compensate each other. It appears more likely that, in consequence of the roughness of solid surfaces, an air-water surface continues underneath the drop so that  $\gamma_{\text{SL}}$  and  $\gamma_{\text{LG}}$  are interdependent.

It also follows from (1) that alteration of  $\gamma_{\text{LG}}$  alone cannot reverse the sign of  $\cos \theta$ , *i.e.* cannot make obtuse a contact angle which is acute, and *vice versa*. In the course of "water-line corrosion" of multilayers (see 2 (a)) angles which immediately after deposition of the drops were *e.g.*,  $101^\circ$  decreased gradually to, *e.g.*,  $59^\circ$  without any discontinuity at  $90^\circ$ . From the point of view of equation (1) this behaviour would suggest that the decay of  $\theta$  is not due to a lowering of  $\gamma_{\text{LG}}$ . It is, however, also possible that equation (1) is not always correct.

### Summary.

(1) A new method of determining large wetting angles is described. It is based on the measurement of the marks left by drops on solid surfaces.

(2) Wetting angles between air, water, and "built-up" multilayers are measured. They confirm the view that Y films are deposited when the

\* Octadecyl amine tends to give Z multilayers.

<sup>6</sup> K. Blodgett, *J. Amer. Chem. Soc.*, 1935, **57**, 1007.

<sup>7</sup> I. Langmuir, *Science*, 1938, **87**, 493.

<sup>†</sup> It may be the surface of a multilayer or of paraffin wax.

angle is near  $90^\circ$ , whilst more hydrophobic surfaces give rise to X, and less hydrophobic ones to Z deposition.

(3) Langmuir's hypothesis connecting wetting angles with molecular orientation, and the usual theory of contact angles are briefly discussed.

The experiments here reported were carried out in the Department of Colloid Science, The University, Cambridge. I thank Professor E. K. Rideal and Dr. J. H. Schulman for suggestions and encouragement, and the Metal Box Co. Ltd. for financial assistance.

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## AN ACCURATE DIRECT READING MANOMETER FOR CORROSIVE AND OTHER GASES.

By R. SPENCE.

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The ordinary U-tube type of mercury manometer is still the most convenient means of measuring gas pressures up to one atmosphere. Extremely accurate results may be obtained if a cathetometer is used and if the proper corrections for temperature and variation of gravitational constant are made. The simplicity, accuracy, and reliability of such instruments fully meet with the requirements of modern gas kinetics. There are, however, several limitations. Firstly, the gases under investigation may react chemically with the manometric liquid, as for example in the case of the halogens. Secondly, the existence of a free mercury surface introduces an additional variable into the reaction system, frequently of major importance, namely, an indeterminate partial pressure of mercury vapour. Thirdly, there is generally a considerable dead-space between the gas reservoir and the surface of the manometric liquid which normally varies with change of pressure. In experiments on gas kinetics, this dead-space must be accurately known.

Various kinds of Bourdon gauge of glass or quartz which avoid some of these difficulties have been in use for many years. The quartz spiral manometer of Bodenstein and Dux<sup>1</sup> has a very small dead-space and when used as a null-instrument is quite accurate. It is, however, rather delicate and is somewhat expensive to make. Moreover, extra time and labour are involved in adjusting the balancing-pressure and reading the manometers. This is sometimes important in a fast reaction. The same considerations apply in the case of the Bourdon spoon gauge, which is, in general, more liable to collapse under sudden changes in pressure. Glass "click" gauges have been used to a considerable extent. They are easy to make but they are very delicate and they require the usual balancing-pressure system. A number of direct reading manometers of glass or quartz have been described, which are in general elaborate and expensive and they do not equal the mercury manometer in regard to range, accuracy, or reliability. As a rule, the movement of a diaphragm or Bourdon coil is shown on a screen or recorded on a photographic film by means of an optical lever.<sup>2</sup> The

<sup>1</sup> Bodenstein and Dux, *Z. physik. Chem.*, 1913, 85, 305.

<sup>2</sup> Lewis and Style, *Nature*, 1937, 139, 631. Lockspeiser, *J. Sci. Instr.*, 1930, 7, 145.



ideal instrument would possess the range of scale, accuracy and dependability of the mercury manometer whilst the gases under investigation would come into contact only with glass or quartz and there would be a negligible or small, constant dead-space.

In the hope of constructing an instrument which would approach more closely to these requirements, some experiments were carried out with glass bellows, and an attempt was made in the first instance to utilise the electronic ultra-micrometer as an indicator. Changes in capacity due to displacements of the order of  $10^{-6}$  cm. can be detected by the ultra-micrometer,<sup>3</sup> and several such instruments have been described which are comparatively stable and which show a linear relationship between voltage or current and displacement.<sup>4</sup> Manometric readings to 0.1 mm. Hg over a range of 1 atm., however, correspond to an accuracy of the order of 0.01 % which unfortunately could not be attained in practice using the

ultra-micrometer. Moreover, a scale of  $10^4$  divisions would involve the use of a potentiometer rather than a galvanometer or ammeter and this would greatly increase the cost and complexity of the apparatus. In the final arrangement, therefore, the glass bellows was filled with mercury as shown in Fig. 1. The bellows was sealed into a close-fitting glass tube and a change of pressure of 1 atmosphere in the annular space produced a displacement of the mercury meniscus in the 1 mm. capillary side tube of about one-fifth of the normal barometric height. The degree of accuracy is therefore about one-fifth of that attainable with the U-tube manometer.

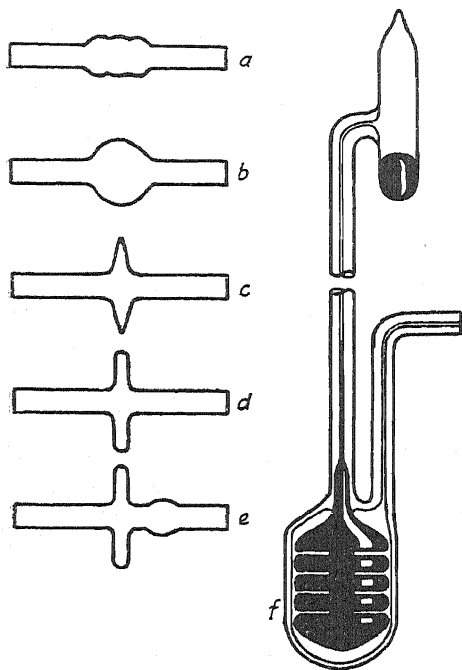


FIG. 1.

to thicken slightly, and then blown out to about 1 cm. diameter. By repeating the process twice, about 1.5 cm. of 1 cm. tubing was produced (Fig. 1a). This was blown to form a larger bulb (Fig. 1b), the wall of which was practically uniform in thickness. Gentle pressure on the ends of the tubing gave a disc (Fig. 1c), which was now blown at the edge to a "pancake" shape (Fig. 1d). A second pancake was produced in exactly the same way (Fig. 1e) not more than 0.5 cm. from the first one, and by directing a very sharp flame on to the short length of connecting tubing, it was gradually thickened and shortened and the bellows were finally pushed close together but without touching at any point. Five such

### Construction.

A length (about 15 cm.) of Pyrex glass tubing (external diameter 0.55 cm., internal diameter 0.35 cm.) was heated in the middle, allowed

<sup>3</sup> Dowling, *Phil. Mag.*, 1923, 46, 81.

<sup>4</sup> Schmidt, *Hochfrequenztechnik und Elektroakustik*, 1933, 41, 96. Spencer-Smith, *J. Sci. Instr.*, 1935, 12, 316.

bellows were completed, one side arm was sealed off, and the end walls were blown out (Fig. 1f) so as to fit the containing tube as closely as possible. It is advisable to test the bellows thoroughly by repeated sudden evacuation on either side. The remainder of the instrument was constructed as shown in Fig. 1f, the interior of the 1 mm. capillary tube being slightly ground to prevent sticking of the mercury. After having been thoroughly cleaned, the instrument was evacuated and filled with highly purified mercury. The level of the mercury column could be adjusted by means of the small reservoir at the top.

### Calibration.

A thermos flask filled with ice forms a convenient means of keeping the bulb at constant temperature and the displacement of the mercury meniscus can be read off on a travelling microscope or cathetometer. There is no detectable hysteresis effect, and exactly the same straight line relationship between pressure and meniscus displacement was obtained again after an interval of four months. The constants of this equation were obtained from the data by the method of least squares.

MANOMETER I. DEAD SPACE 8.75 c.c.

EQUATION:  $p_{\text{cm. Hg}} = 5.02d \text{ cm.} - 16.71$ .

$d$ .	$p_{\text{obs.}}$	$p_{\text{calc.}}$
16.320	65.26	65.21
13.460	50.85	50.86
10.014	38.01	38.07
8.468	25.81	25.80
5.880	12.82	12.81
4.236	4.55	4.55

The travelling microscope used gave readings accurate to 0.05 mm. corresponding to 0.25 mm. Hg. Visual readings of the mercury U-manometer have about the same degree of accuracy so that the agreement between  $p_{\text{obs.}}$  and  $p_{\text{calc.}}$  can be regarded as satisfactory. A finer and more uniform capillary and a good cathetometer would, of course, considerably improve the accuracy.

If set up in the same way as an accurate thermometer, with enclosed scale, calibrated at 0°, the manometer could be used as a direct-reading instrument. Visual readings to 0.2 mm. would be accurate to 1 mm. Hg. which is sufficient for many purposes. The instrument possesses the advantage of comparatively small size, the movement of the mercury meniscus is practically instantaneous and free from oscillation, whilst pressure measurement involves only a single scale reading. Although designed primarily for work involving chemically reactive gases, it should also find useful application in the case of inert gases.

### Summary.

A glass manometer is described in which the relation between scale reading and pressure is linear. The dead space is small and practically constant (variation 1.25 % for 1 atm). and pressures up to 1 atmosphere can be readily determined to within 0.25 mm. Hg. The instrument is specially suited for the study of gas reactions.

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# THE PROPERTIES OF DETERGENT SOLUTIONS. PART X. SOME FURTHER OBSERVATIONS ON ELECTROPHORETIC MOBILITIES IN DE- TERGENT SOLUTIONS.

BY J. POWNEY AND L. J. WOOD.

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In a previous paper<sup>1</sup> we described some measurements of the electrophoretic mobility of mineral oil (Nujol) in alkalis and in solutions of certain surface-active substances. This work has now been extended to include the study of the influence of temperature, chain-length and added electrolytes on the electrophoretic mobility. In addition to oil drops, suspensions of wax, ilmenite and calcium laurate have been investigated. The experimental technique was the same as that used in the previous investigation except that the electrophoresis cell and microscope were placed in an air thermostat to enable measurements to be made at higher temperatures.

## Results and Discussion.

### Influence of Temperature and Chain-Length.

In considering the influence of temperature upon electrophoretic mobilities in solutions of paraffin chain salts the following factors have to be taken into account :

- (a) change of viscosity of the dispersion medium,
- (b) change of state of aggregation of the solution,
- (c) change of degree of adsorption of the long chain ions.

The second and third factors have also to be considered in connection with the effect of chain-length on mobilities.

For particles suspended in water Freundlich<sup>2</sup> has pointed out that the change of mobility with temperature should depend only on the change of viscosity of the water according to the simple relationship  $u_1\eta_1 = u_2\eta_2$ , where  $u$  represents the mobility of the particle and  $\eta$  the viscosity of the water. In the present work it has been confirmed that this holds for suspensions of Nujol and paraffin wax in water over the temperature range 25° to 60°.

The abrupt transition from single ions to micelles which occurs in solutions of paraffin chain salts at certain critical concentrations is reflected in a sudden change of properties such as density, electrical conductivity, surface and interfacial activities. The critical concentrations at which these changes occur are known to depend on temperature and chain-length.<sup>3</sup> The preliminary data given in the previous paper<sup>1</sup> showed that the aggregation to form ionic micelles is also reflected in the electrophoretic behaviour of oil drops dispersed

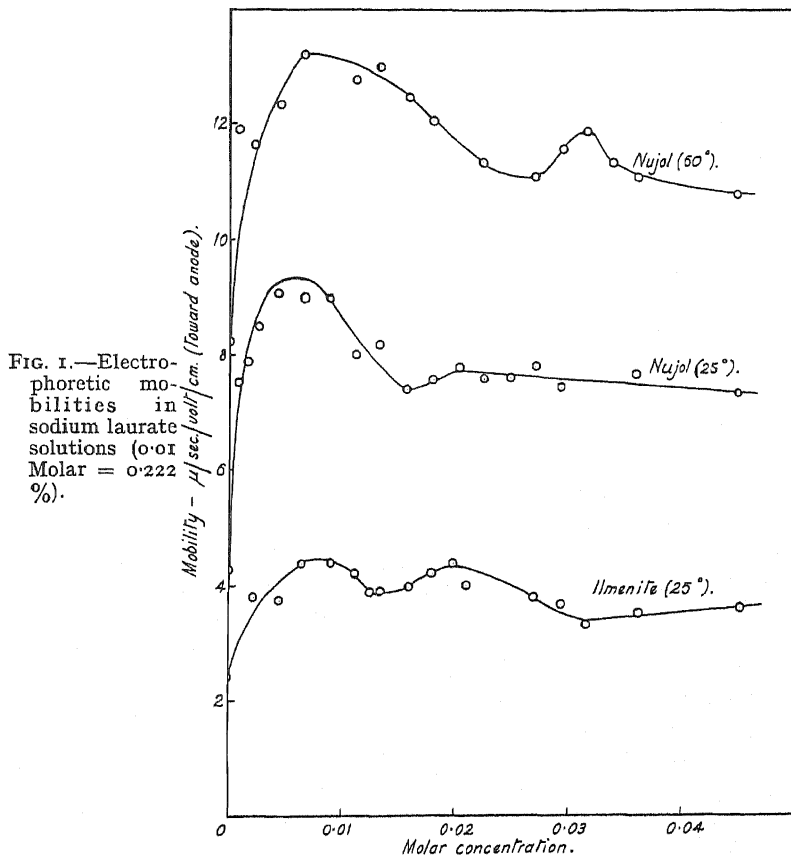
<sup>1</sup> Powney and Wood, *Trans. Faraday Soc.*, 1940, **36**, 57.

<sup>2</sup> Freundlich, *Colloid and Capillary Chemistry*, London, p. 248.

<sup>3</sup> Cf. Hartley, *Aqueous Solutions of Paraffin-chain Salts*, Paris, 1936.

in such solutions. The additional mobility data now obtained confirm that the critical concentration rises with decreasing chain-length and increasing temperature.

The mobilities of oil drops in sodium laurate solutions at 25° and 60° C. are shown in Fig. 1 together with data for ilmenite ( $\text{FeO} \cdot \text{TiO}_2$ ) particles in similar solutions at 25° C. The commencement of aggregation of the laurate ions is indicated by minima which occur at a concentration of approximately 0.35 % at 25° C. and 0.6 % at 60°. The view that these minima are related to a sudden change in constitution of the sodium laurate solution is supported by the fact that the minima



for both Nujol and ilmenite, two very different types of particles, occur at similar concentrations. Inflections in the curves are also shown by Nujol in sodium myristate and sodium palmitate solutions at 60° C. (Fig. 2) at concentrations which decrease with increasing chain-length. The minimum in the sodium palmitate curve is at a somewhat higher concentration than might be anticipated from available data for the critical concentrations of unhydrolysed paraffin chain salts of similar chain-length. This is undoubtedly due to the fact that sodium palmitate is considerably hydrolysed in solution<sup>4</sup> at 60°.

<sup>4</sup> Powney and Jordan, *Trans. Faraday Soc.*, 1938, **34**, 363.

For an unhydrolysed long chain salt such as sodium tetradecyl sulphate (Fig. 3, *a* and *b*) the inflections in the mobility curve also occur very close to the critical concentration as determined from surface and

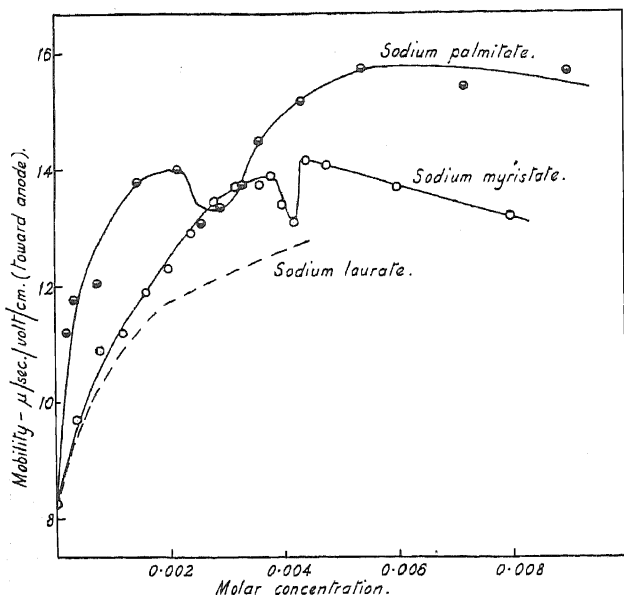


FIG. 2.—Electrophoretic mobilities of Nujol in sodium myristate and sodium palmitate solutions at 60° C.

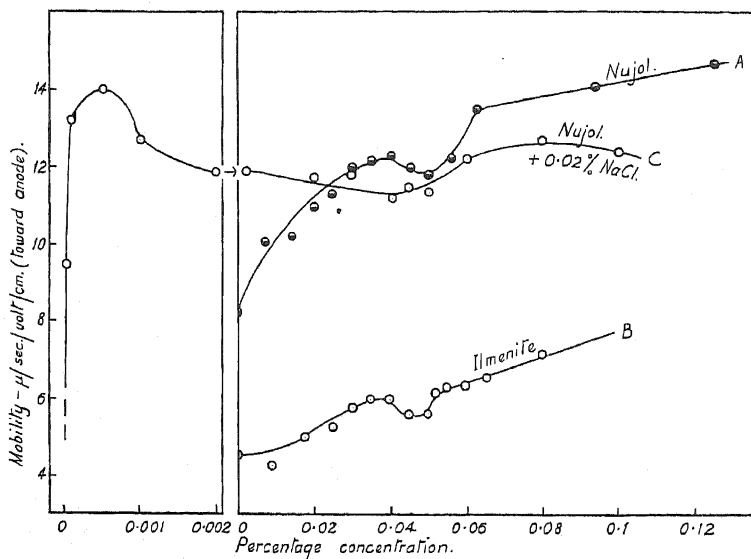


FIG. 3.—Electrophoretic mobilities in sodium tetradecyl sulphate solutions at 60° C.

interfacial tension and conductivity data.<sup>5</sup> As was found with sodium laurate, the nature of the particle does not in any way determine the position of the mobility minimum.

<sup>5</sup> Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243, and 1938, **34**, 372.

Since it is highly probable that the increase in the mobility of oil drops on the addition of paraffin chain salts is due to the adsorption of long chain ions, increase of temperature will indirectly affect the mobility by decreasing the degree of adsorption. Thus, for Nujol in sodium laurate solutions at 60° C. the observed mobilities are only about 75 % of the values calculated from corresponding data determined at 25° on the assumption that change of viscosity is the only factor. This difference is probably due to a decrease in the adsorption of laurate ions at the higher temperature, as check measurements show that the viscosity of paraffin chain salts at the concentrations used in this investigation does not differ from that of water at the same temperature by more than 1 %. A negative temperature coefficient of adsorption of long chain ions is also indicated by surface and interfacial tension measurements.<sup>5</sup>

The general effect of increase of chain-length is to give rise to somewhat higher values of mobility, particularly in very dilute solutions. This is shown by the data for sodium laurate, myristate, and palmitate given in Fig. 2 and can be attributed to an increase in the degree of adsorption of the long chain ions rather than to any specific influence of chain-length upon the effective charge of the adsorbed ions. The mobility of carbon particles in soap solutions has been found by Urbain and Jensen<sup>6</sup> to increase with increasing chain-length, but their observations have been confined to a single concentration (0.0036 molar) which in some instances is above and in others below the critical concentrations of the long chain salts.

### Influence of Added Electrolytes.

In our previous discussion<sup>1</sup> of the mobility of Nujol in solutions of paraffin chain salts we described the sharp change in the region just below the critical concentration and attributed it to a superimposed sodium ion effect. It was thought of interest to determine whether increasing the concentration of sodium ions in the solution by the addition of NaCl would lead to a general decrease of mobility. A series of experiments was made in which 0.02 % of NaCl was added to solutions of sodium tetradecyl sulphate,  $C_{14}H_{29}SO_4Na$  (Fig. 3c). For concentrations of  $C_{14}H_{29}SO_4Na$  above 0.03 %, the addition of the NaCl results in a decrease of mobility. Below 0.03 %, however, the mobility is considerably increased by the addition of NaCl and at a concentration of 0.0005 %  $C_{14}H_{29}SO_4Na$  has the remarkably high value of  $14\mu/\text{sec./volt/cm.}$  With 0.00002 %  $C_{14}H_{29}SO_4Na$  the mobility is 10, a figure only attained at a concentration of 0.01 % in the absence of sodium chloride. The values at low concentrations were obtained by successive dilutions of the emulsions with the stock aqueous Nujol emulsion and with NaCl so as to keep the concentrations of both of these constant. The persistently high mobilities could not be due to any time factor in attaining adsorption equilibrium since at each dilution at least an equal amount of Nujol was added and therefore at least half the Nujol droplets in the new mixture were freshly added to the surface active solution. No irregularities outside the usual experimental error were found in the mobilities of the individual Nujol droplets.

These high values are all the more surprising since the addition of

<sup>6</sup> Urbain and Jensen, *J. Physic. Chem.*, 1936, 40, 821.

NaCl to Nujol in pure water causes a considerable decrease in mobility.<sup>1</sup> Neutral salts are known to increase the interfacial activity of paraffin chain salt solutions,<sup>7</sup> and it is possible that the high mobilities are due to an increased adsorption of long chain ions at the surface of the oil

TABLE I.

NaCl (%)	Mobility ( $\mu$ /sec./volt/cm.).
Zero	8.4 *
0.001	9.2
0.005	10.4
0.02	12.3
0.05	13.5
0.1	13.3

\* By interpolation from Fig. 3a.

drops. The interfacial activities of the extremely dilute solutions of sodium tetradecyl sulphate used are, however, quite low and would not appear to account entirely for the very high electrophoretic mobilities observed under similar conditions. In the first part of this investigation<sup>1</sup> it was also shown that the high mobility of Nujol in very dilute solutions of the cation-active salt dodecyl pyridinium chloride could not be correlated with the interfacial activity of the solution.

A further series of measurements was carried out to determine the quantity of sodium chloride necessary to produce an optimum effect at a low concentration (0.001 %) of  $C_{14}H_{29}SO_4Na$ .

These are given in Table I and indicate that 0.02 to 0.05 % sodium chloride is necessary.

### Influence of Nature of Particle.

(a) **Liquid and Solid Paraffin.**—Since the mobility of liquid paraffin in surface active solutions is dependent upon the formation of oriented interfacial films of long chain ions, it was thought of interest to investigate whether a transition of the particle from the liquid to the solid state would influence its mobility, possibly by effecting a change in the degree or in the nature of the adsorption. For this purpose a series of measurements on a sample of paraffin wax (congealing point  $49^\circ$ ) in 0.1 %  $C_{14}H_{29}SO_4Na$  was made at increasing temperatures from  $37^\circ$  to  $60^\circ$ . The data obtained are shown in Table II and it will be noted that no significant changes of mobility occur at the melting-point of the wax. The product  $u\eta$ , where  $\eta$  is the viscosity of the dispersion medium in centipoises, shows a small but definite decrease with increasing temperature of the same order as was found with Nujol in sodium laurate solutions described above.

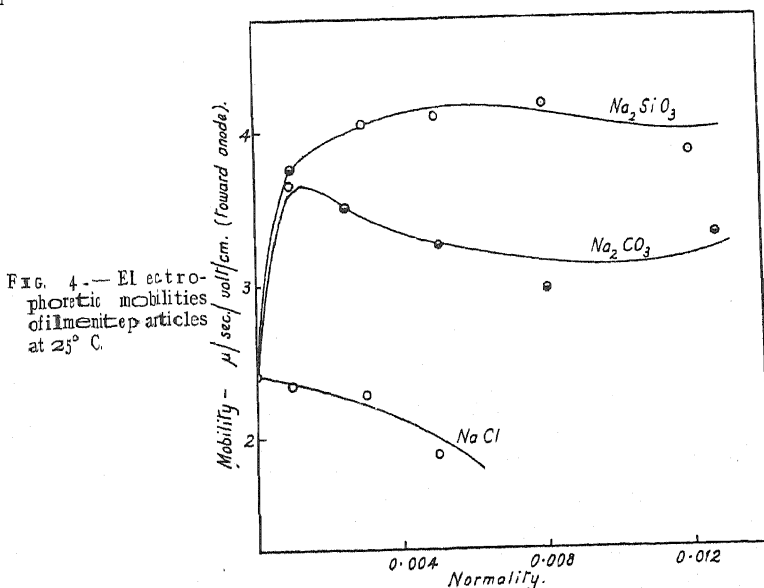
TABLE II.

Temperature ( $^\circ C.$ )	Mobility ( $\mu$ /sec./volt/cm.).	$\eta$ .	$u\eta$ .
37.1	11.5	0.69	7.9
42.1	12.2	0.63	7.7
45.7	12.3	0.59	7.3
50.5	13.2	0.54	7.2
55.5	13.2	0.50	6.6
59.7	14.6	0.47	6.9

(b) **Calcium Laurate.**—The mobility of another type of particle, namely calcium laurate, has been studied and the value for a suspension in water at  $25^\circ C.$  found to be  $3.8 \mu$ /sec./volt/cm. towards the anode, which is approximately the same as that found for other hydrophobic particles such as Nujol and paraffin wax.

<sup>7</sup> Robinson, *Wetting and Detergency*, London, 1937, p. 137, and Powney and Addison, *Trans Faraday Soc.*, 1937, **33**, 1253.

(c) **Ilmenite.**—The behaviour of ilmenite particles in sodium laurate and sodium tetradecyl sulphate solutions has been mentioned above and is illustrated in Figs. 1 and 3. A stock suspension was prepared in the following manner. A sample of "Air-floated Ilmenite Black," supplied by Messrs. British Titan Products Co., Ltd., was first treated with sodium hexametaphosphate to remove traces of divalent metal salts which were found to be present. The ilmenite was then thoroughly washed with conductivity water and dried. Two grams of the material were shaken up with a litre of conductivity water and allowed to stand for 4½ hours. About 700 c.c. were then carefully decanted and kept as the stock suspension. For use it was diluted with an equal volume of a solution of alkali or detergent. The particles had a diameter of approximately 1.2  $\mu$ . The mobility of ilmenite particles suspended in water is approximately half that of oil drops in water and this ratio persists in sodium laurate and sodium tetradecyl sulphate solutions



at all the concentrations examined. It might have been expected that at the higher concentrations where the surfaces are probably fairly well covered with long chain ions the potential of the particles would be dependent only on the charge of the ions and independent of the nature of the "core" of the particle. At any given temperature, however, the mobility of ilmenite in solutions of paraffin chain salts attains but never rises above the water value for hydrophobic particles such as Nujol. A tentative explanation is that in the case of ilmenite particles the long chain ions are oriented in the opposite direction to those on oil drops, i. e., the polar heads will be oriented towards the ilmenite surface leaving the particles as a whole with a hydrophobic exterior of hydrocarbon chains, the resulting mobility being that found for an oil drop. It is not clear why the mobility is not further increased by the adsorption of a second long chain ion film to give a value characteristic of a normal oil drop in paraffin chain salts solutions. This may possibly be due to some restriction in the formation of a bimolecular film.



Some measurements have also been made of the mobility of ilmenite in sodium chloride, sodium carbonate and sodium metasilicate solutions and the results are plotted in Fig. 4. These are qualitatively the same as those obtained for Nujol in similar solutions and described in our previous paper.<sup>1</sup> The mobility rises rapidly with increasing hydroxyl ion concentration but is lowered slightly by increasing sodium ion concentration. Although there are slight divergences there is again a tendency for the ilmenite particles to have one-half the mobility of Nujol drops under the same conditions.

### Summary.

Additional data concerning the electrophoretic mobility of oil drops in solutions of paraffin chain salts are recorded. The maximum mobilities in such solutions are obtained at concentrations which decrease with increasing chain-length. The abrupt changes of mobility which occur in the region of the critical concentration of the paraffin chain salt are discussed.

The change of mobility with increasing temperature is dependent not only upon change of viscosity of the dispersion medium but also upon changes in the degree of adsorption of the long chain ions at the interfaces.

The mobility of Nujol in sodium tetradecyl sulphate solutions of concentration greater than 0.03 % is depressed by the addition of NaCl. At lower concentrations of the paraffin chain salt, however, the added electrolyte produces a considerable increase of mobility. Thus, on the addition of 0.02 % NaCl to 0.0005 %  $C_{14}H_{29}SO_4Na$  at 60° C. the mobility rises from 8.3 to 14  $\mu$ /sec./volt/cm., a value only attained at two hundred times this concentration in the absence of NaCl.

The mobilities of ilmenite, calcium laurate and paraffin wax have also been determined and the results are discussed in connection with the influence of nature of particle on mobility.

The authors wish to thank the Director of Research for his valuable advice, and the Council of the British Launderers' Research Association for permission to publish this work.

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### REVIEW OF BOOK.

**Chemical Spectroscopy.** By W. R. BRODE. (Chapman & Hall, 1939.) Pp. xii + 494. Price 36s. net.

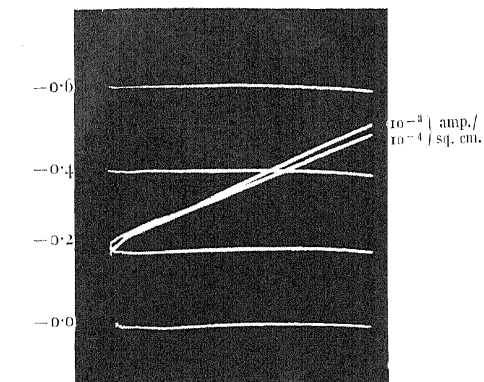
This should prove a useful book for students whose interests are in spectroscopy as a "profession." This activity exists in the United States to a degree not always appreciated in this country.

Judged by these standards, the distribution of subjects—absorption, emission, qualitative and quantitative analysis and so forth—is probably correct. Much the same applies to the instrumental sections, where apparatus is described in detail. Throughout, the aim seems to me to give the reader information of considerable precision within a very limited range of ideas.

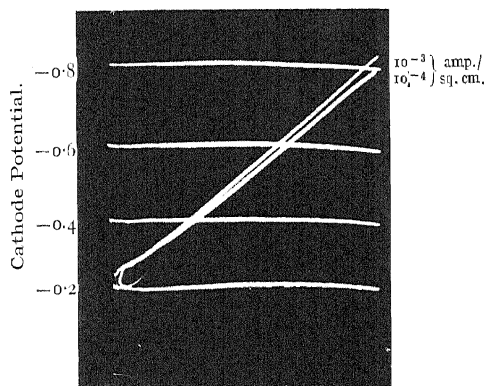
As a laboratory guide, the volume can be recommended.

F. I. G. R.

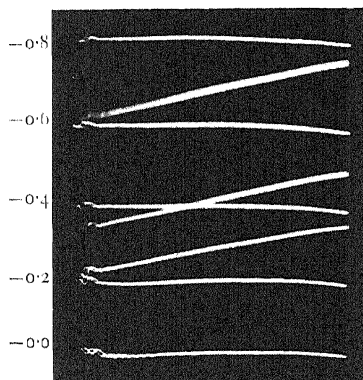
PLATE V.



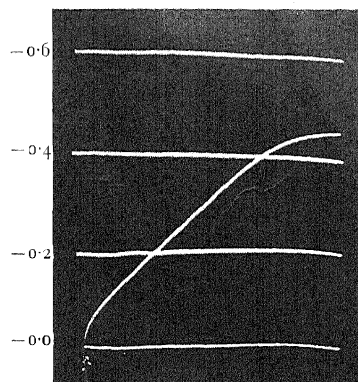
A



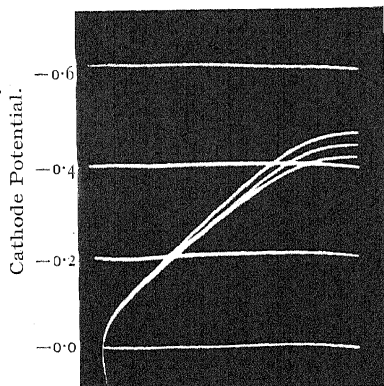
B



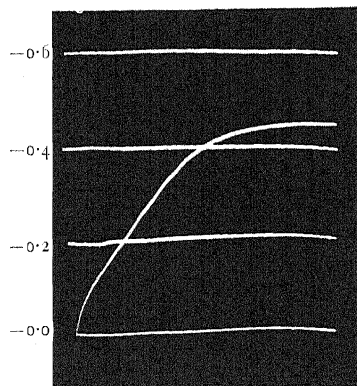
C  
Quantity of Electricity.  
FIG. 3.



A



B



C  
Quantity of Electricity.  
FIG. 4.

[See page 367.]

PLATE VI.

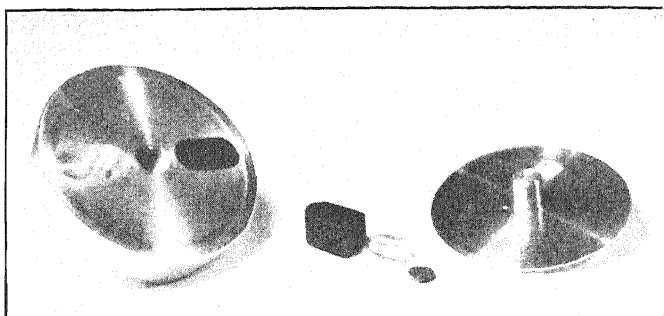


FIG. 1.—Photograph of rotor, showing cell and hard rubber block.  
[See page 381.]

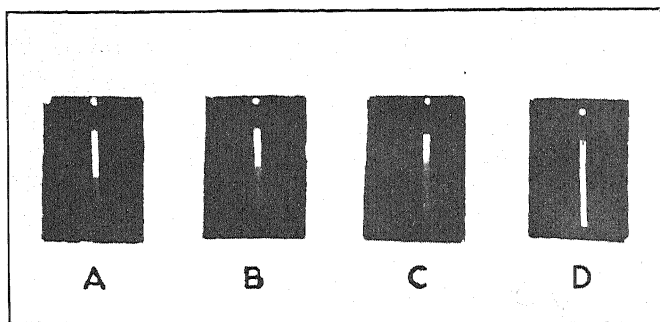


FIG. 4.—A, B, sedimentation of erythrocrucrin of earthworm blood ; C, carboxyhemoglobin, and D, half-concentration, about 0.5 %, of carboxyhemoglobin (boundary near top of liquid).

[See page 384.]

# ON THE FLUORESCENCE AND ABSORPTION SPECTRA OF ANTHRACENE AND PHENANTHRENE IN SOLUTIONS.

By S. SAMBURSKY AND G. WOLFSOHN.

*Received 17th July, 1939.*

The fluorescence and absorption spectra of anthracene and phenanthrene have been investigated in different solvents,<sup>1</sup> but the wave-length maxima measured by various authors differ appreciably. Most authors assume that both absorption and fluorescence spectra are displaced by a given wave-number in each solvent, when compared with the spectrum in the gaseous state. Banerjea and Mishra,<sup>2</sup> on the other hand, claim that the relative positions of the maxima vary with the solvent, and that the frequency differences between the absorption and the emission maxima can be related to the Raman frequencies of the solvent; according to the general opinion, however, the differences between absorption and fluorescence spectrum in solvents arise as follows<sup>3</sup>: the molecules in the vibrational levels of the excited electronic state revert to the zero level of the excited state without radiation; from this level the molecules then return to the various vibrational levels of the lower electronic state, emitting the fluorescence spectrum. From this mechanism it may be predicted that the frequency differences of the fluorescence spectrum will exhibit vibrational frequencies of the ground state. On the other hand, more recent investigations<sup>4</sup> of the spectra of benzene have shown that in the gaseous state the vibrational levels of the excited electronic state are also involved in the production of the fluorescence spectra.

The object of the present investigation was to measure accurately the absorption and fluorescence spectra of anthracene and phenanthrene in different solvents in order to obtain definite information as to the mechanism of absorption and emission processes in solutions.

## Experimental.

Fluorescence was measured by two methods: (1) In the usual arrangement: fluorescence tube and Hg lamp parallel; the observations were made end-on.

(2) A reduced image of a vertical arc Hg lamp was thrown immediately behind the window of the quartz cell containing the solution. Thus only the foremost layer of the solution was allowed to throw fluorescence light on the slit of the spectrograph. A filter containing approximately 15 % NiCl<sub>2</sub> solution was inserted between light source and fluorescence cell.

<sup>1</sup> D. Radulescu and C. Dragulescu, *Bull. Soc. Chim. Rumania*, 1936, **17**, 9; P. K. Seshan, *Proc. Ind. Acad., Sc. A*, 1936, **3**, 148; *Trans. Faraday Soc.*, 1936, **32**, 689; A. A. Shishlovskij, *Compt. Rend. Acad. Sc. URSS.*, 1937, **15**, 29; P. Pringsheim, *Trans. Faraday Soc.*, 1939, **35**, 15. (For earlier data see Shishlovskij, *loc. cit.*)

<sup>2</sup> G. B. Banerjea and B. Mishra, *Z. Physik*, 1937, **106**, 669.

<sup>3</sup> E. J. Bowen, *Trans. Faraday Soc.*, 1939, **35**, 15.

<sup>4</sup> Sponer, Nordheim, Sklar and Teller, *J. Chem. Physics*, 1939, **7**, 207.

By suitable adjustment of the cell no geometrically reflected light could reach the spectrograph. The light intensity in this arrangement is smaller than in the former, but there is practically no absorption of fluorescence light by the solution and no influence on the position and intensity of the fluorescence maxima extending into the absorption region. The fluorescence bands of anthracene were photographed with a Hilger spectrograph ( $f = 1$  m.); the absorption bands of anthracene and the spectra of phenanthrene were photographed with a single-prism quartz spectrograph ( $f = 60$  cm.). A standard tungsten band lamp with a quartz window provided a source of heterochromatic density marks, from which we could calculate the intensities by measuring the density marks and the spectra by a Moll microphotometer. Purified anthracene (Kahlbaum) and phenanthrene (B.D.H.) were used. The latter contained traces of anthracene (as was evident from the absorption spectrum) which were completely removed by purification according to the method of Clar.<sup>5</sup> Pure phenanthrene does not fluoresce in the visible, and the blue fluorescence described in the literature is due to the presence of anthracene. The absorption bands 3750 Å and 3560 Å frequently attributed to phenanthrene<sup>6</sup> are also due to anthracene.

The continuous spectrum of a hydrogen discharge tube was used as light source for the absorption measurements. The current was kept constant and the continuous light was used for taking the density marks. Anthracene was investigated in a concentration of  $1 \times 10^{-4}$  to  $3 \times 10^{-5}$  mol./l.; phenanthrene in concentrations of  $5 \times 10^{-4}$  to  $1 \times 10^{-4}$  mol./l. The fluorescence yield of anthracene reaches its maximum at about  $2 \times 10^{-4}$  mol./l. In higher concentrations the mutual interaction of fluorescent molecules leads to extinction, and this probably effects also the position of the band maxima.

## Results.

### 1. Anthracene.

The mean intensity curve of the fluorescence spectra of anthracene in benzene, toluene, chlorobenzene, methanol and hexane solutions.

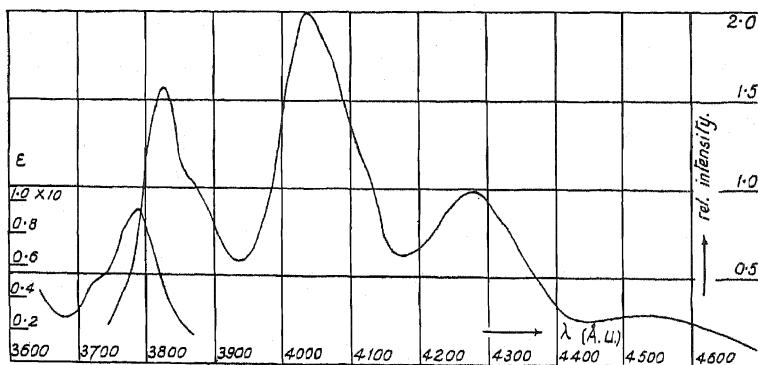


FIG. 1.—Intensity curve of the fluorescence spectrum of anthracene in benzene solution.

(On the left side the first absorption band is drawn in order to illustrate its position relative to the ( $\sigma'$ ,  $\sigma$ ) fluorescence band. The ordinates on the left give the absorption coefficient  $\epsilon$  (mol.<sup>-1</sup> lit. cm.  $\times 10^4$ .)

respectively is given in Fig. 1. The spectra in these solvents are displaced relatively to each other, but the form of all the curves is identical

<sup>5</sup> E. Clar, *Ber.*, 1932, **65**, 846.

<sup>6</sup> W. V. Mayneord and E. M. F. Roy, *Proc. Roy. Soc.*, 1935, **152**, 299; Landolt-Börnstein. *Tab. 2. Aufl.*, 1923, 901.

within the limits of the experimental error. It is evident from Fig. 1 that in addition to the constant vibration frequency  $1380\text{ cm.}^{-1}$  of the ground state, the vibration bands also show secondary periodicities ( $\text{frequency } 225\text{ cm.}^{-1}$ ) in the long wavelength side. Approximately the same periodicities are found in the short wavelength side of the absorption bands. The principal frequency difference in absorption corresponding to the excited state ( $1425\text{ cm.}^{-1}$ ) is slightly greater than that of the ground state. The fluorescence spectrum of anthracene in solutions can be expressed in the form

$$\nu = \nu_0 - 1380n - 225p,$$

$n$  and  $p$  being integers;  $\nu_0$  for the different solvents can be found in the first line of Table I.

The most characteristic feature of the fluorescence spectrum of benzene is the frequency  $991\text{ cm.}^{-1}$  which corresponds to the totally symmetrical C-vibration of the molecule.<sup>7</sup> The frequency  $1380\text{ cm.}^{-1}$  is but slightly smaller than the totally symmetrical Raman vibration  $1400\text{ cm.}^{-1}$  of anthracene found by Manzoni Ansidei,<sup>8</sup> and probably identical with the latter, whereas the frequency  $225\text{ cm.}^{-1}$  does not appear in the Raman spectrum of anthracene. In view of the smallness of this frequency it is doubtful whether it can be regarded as a fundamental one. The secondary maxima due to  $225\text{ cm.}^{-1}$  appear in absorption and emission on

TABLE I.—MAXIMA OF THE ANTHRACENE BANDS IN DIFFERENT SOLVENTS.

Solvent:	Hexane.			Methanol.			Toluene.			Benzene.			Chlorobenzene.		
	Transi- tion.	Rel. Int.	$\lambda$ .	$\nu$ .	$\Delta\nu$ .	$\lambda$ .	$\nu$ .	$\Delta\nu$ .	$\lambda$ .	$\nu$ .	$\Delta\nu$ .	$\lambda$ .	$\nu$ .	$\Delta\nu$ .	$\lambda$ .
(a) Fluorescence.															
(0', 0')		1.6	3770	26,517	1384	3778	26,461	1387	3820	26,170	1376	3828	26,116	1383	3835
(0', 1')		2.0	3978	25,131	1385	3987	25,074	1384	4032	24,794	1382	4042	24,733	1375	4050
(0', 2')		1.0	4210	23,746	1381	4220	23,690	1375	4270	23,412	1372	4280	23,358	1372	4290
(0', 3')		0.3	4470	22,365		4480	22,315		4536	22,040		4547	21,986		4561
(b) Absorption.															
(0, 0')			3748	26,673	1424	3753	26,638	1436	3787	26,398	1426	3790	26,378	1423	3795
(0, 1')			3558	28,097	1427	3561	28,074	1433	3593	27,824	1433	3596	27,801	1430	3600
(0, 2')			3386	29,524	1426	3388	29,507	1434	3417	29,257	1428	3420	29,231	1426	3424
(0, 3')			3230	30,950		3231	30,941		3258	30,685		3261	30,657		3265

<sup>7</sup> C. K. Ingold and A. Wilson, *J. Chem. Soc.*, 1936, 941.

<sup>8</sup> R. Manzoni Ansidei, *Rend. Linc.*, 1936, 24, 368.

opposite sides of the main maxima. In contrast to this, in the case of benzene the secondary maxima due to the frequency  $160\text{ cm}^{-1}$  appear on the same side of the main maxima. Therefore we must conclude that the frequency  $225\text{ cm}^{-1}$  in anthracene is not analogous to the frequency  $160\text{ cm}^{-1}$  for benzene, which corresponds in fact to a series of  $n$ - $n$  transitions of a vibration whose frequency in the excited state has dropped by  $160\text{ cm}^{-1}$ .

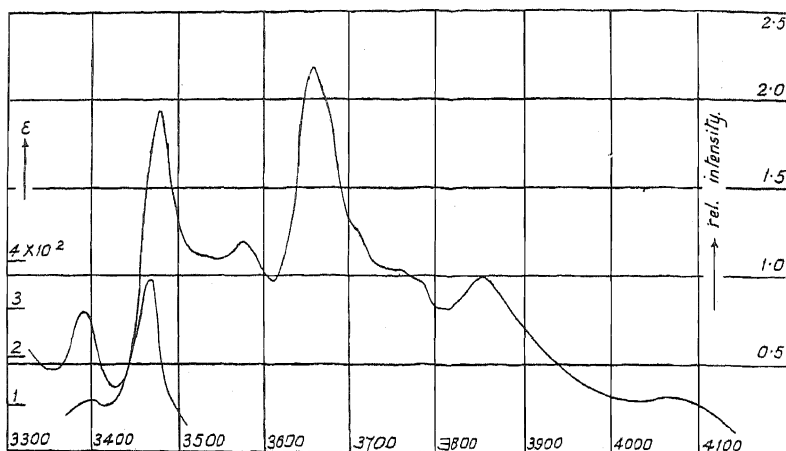


FIG. 2.—Intensity curve of the fluorescence spectrum of phenanthrene. (On the left side the first absorption bands are drawn.)

The figures of Table I show clearly that the hypothesis of Banerjee and Mishra is untenable. Almost the same  $\Delta\nu$  appears both in fluorescence and absorption in all solvents. There is no connection between the differences of fluorescence and absorption frequencies and the Raman frequencies of the solvent. In the work of Banerjee and Mishra such a relationship is based on a value for the  $(0, 0)$  fluorescence band which is markedly shifted towards the red by absorption (in benzene by  $320\text{ cm}^{-1}$ ).

## 2. Phenanthrene.

The mean intensity curve of the fluorescence spectra of phenanthrene in benzene and methanol solutions is shown in Fig. 2. As in the case of anthracene, the bands in benzene solution show a shift towards the longer frequencies, when compared with the bands in methanol solutions. Assuming that the excited electronic state consists of two levels and the transitions occur as indicated in Fig. 3, the observed spectra can be easily understood. Absorption measurements made in methanol at temperatures of  $-80^\circ\text{C}$ . and  $+100^\circ\text{C}$ . showed no influence on the intensity of the two alternating band systems, which proves that the two systems are due to splitting up of the excited electronic level. In Table II the data for phenanthrene are given. As in the case of anthracene there appears in emission a constant vibration frequency which is probably also in this

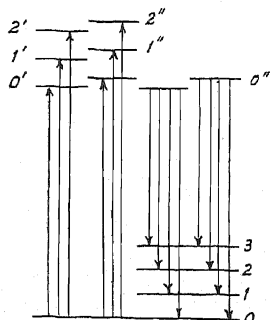


FIG. 3.—Term scheme of the phenanthrene spectra.

case the totally symmetrical Raman frequency. This frequency ( $1346 \text{ cm.}^{-1}$ ), according to Manzoni Ansidei,<sup>8</sup> is somewhat smaller than the difference  $1380 \text{ cm.}^{-1}$  found here. A slight asymmetry in the long wave-length side of the stronger bands indicates the existence of a secondary frequency corresponding to the  $225 \text{ cm.}^{-1}$  frequency of anthracene. As the term scheme in Fig. 3 reveals, the first emission band  $0-0$  ( $\lambda 3405 \text{ \AA}$ ) is already situated in the region of absorption. The intensity ratio of the two systems is 1.3 : 1 in absorption and about 3 : 1 in emission. The determination of the latter ratio is made difficult by the influence of the stronger bands on the peak intensities of the

TABLE II.—MAXIMA OF THE PHENANTHRENE BANDS IN DIFFERENT SOLVENTS.

Solvent :		Benzene.			Methanol.		
Transi- tion.	Rel. Int.	$\lambda$ .	$\nu$ .	$\Delta\nu$ .	$\lambda$ .	$\nu$ .	$\Delta\nu$ .
(a) Fluorescence.							
$(o', o)$	2.0	3480	28,727		3463	28,868	
$(o', 1)$	2.2	3656	27,344	1383	3637	27,487	1381
$(o', 2)$	0.8	3852	25,953	1391	3830	26,101	1385
$(o', 3)$	0.3	4068	24,575	1378			
$(o'', o)$	0.3	3405	29,360	1380	3556	28,113	1383
$(o'', 1)$	0.7	3573	27,980	1378	3740	26,730	
$(o'', 2)$	0.3	3758	26,602				
(b) Absorption.							
$(o, o')$		3469	28,818		3458	28,910	
$(o, 1')$		3308	30,221	1403	3298	30,313	1403
$(o, 2')$		3160	31,636	1415	3151	31,727	1414
$(o, o'')$		3392	29,473		3381	29,568	
$(o, 1'')$		3237	30,883	1410	3228	30,970	1402
$(o, 2'')$		3095	32,301	1418	3088	32,374	1404

weaker ones. The fluorescence spectrum of phenanthrene can be expressed in the form

$$\nu = \left. \begin{matrix} \nu_0' \\ \nu_0'' \end{matrix} \right\} - 1380 n,$$

$$\nu_0'' - \nu_0' = 630 \text{ cm.}^{-1}.$$

$\nu_0'$  and  $\nu_0''$  for the different solvents are given by the  $(o', o)$  and  $(o'', o)$  transitions of Table II.

### 3. Effect of Solvents on the Spectra.

Effects of solvents on the spectra of solutes are known and shown clearly by comparison of the spectra obtained in the dissolved state with that in the vapour state. The former are shifted towards the red approximately by equal wave-numbers both in absorption and fluorescence. The same effect is also shown in the present measurements. (See column 1, Table III.) A second effect which seems to be correlated to the shift but has received little attention up to date, is the frequency difference of the  $(o, o)$  band in emission and absorption (column 2,



Table III). Only in the vapour state is there complete identity in the position of the (o, o) bands in fluorescence and absorption.\* The observed frequencies of the (o, o) bands in solutions of anthracene and phenanthrene are higher in absorption than in emission. This effect

TABLE III.—INFLUENCE OF THE SOLVENT ON THE SPECTRA OF ANTHRACENE.

Solvent.	(1)		(2)
	$\nu_{\text{hexane}} - \nu_{\text{solvent}}$		$\nu_{[o,o']} - \nu_{[o',o]}$
	Fluor.	Abs.	
Hexane . .	—	—	156
Methanol . .	56	22	177
Toluene . .	339	270	228
Benzene . .	395	331	262
Chlorbenzene . .	446	331	275

may be explained as follows: Although the non-excited molecules of phenanthrene and anthracene have no dipole moment, it may be supposed that a dipole moment is formed by excitation. In general, the direction of this dipole moment will differ from the direction of the internal field of the solvent, and the interaction energy between

the field and the dipole will be greater than  $kT$ . This interaction energy is transferred to the field before radiation occurs, and therefore the energy difference is smaller in emission than in absorption. Assuming that the internal field <sup>9</sup> in the solvent is about  $10^7$  V./cm., and the dipole moment of the excited molecule of the solute  $10^{-18}$  c.g.s. units, an interaction energy of the order of  $100 \text{ cm.}^{-1}$  results, in good agreement with the figures in Table III. On this assumption spectroscopic estimation of dipole moments of excited molecules is made possible.

### Summary.

Photographic-photometrical measurements of the fluorescence and absorption spectra of anthracene and phenanthrene in different solvents lead to the following conclusions:

(1) The vibrational bands of the fluorescence spectra of anthracene and phenanthrene in all solvents have a constant spacing of  $1380 \text{ cm.}^{-1}$ , corresponding closely to the totally symmetrical Raman frequencies of these substances.

(2) Anthracene shows a secondary spacing of  $225 \text{ cm.}^{-1}$  which cannot be correlated to a known Raman- or infra red-frequency of this molecule.

(3) The excited electronic state of phenanthrene is double, the difference between these levels being  $630 \text{ cm.}^{-1}$ .

(4) The (o, o) bands in emission and absorption do not coincide, the frequency being larger in the latter. The spacing depends on the nature of the solvent and can be attributed to the energy of interaction between the inner electric field of the solvent and the electric moment of the excited molecules of the solute.

The authors wish to thank Mrs. Th. Wolfsohn for her valuable help in the course of this investigation, and to acknowledge their gratitude to the trustees of the Elizabeth Thompson Science fund for defraying the cost of the comparator used for the wave-length measurements.

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\* For benzene cf. references given in (7).

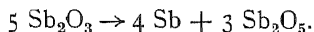
<sup>9</sup> P. Debye, *Chem. Rev.*, 1936, 19, 171.

# THE PHOTOCHEMISTRY OF ANTIMONY OXIDE.

BY G. COHN AND C. F. GOODEVE.

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The sensitivity to light of antimony trioxide when in contact with organic compounds has been observed several times in the laboratory and is well known in the paint trade. Renz<sup>1</sup> found that  $\text{Sb}_2\text{O}_3$  mixed with glycerol turned dark greyish brown when illuminated with sunlight. Later<sup>2</sup> he found a slight photochemical darkening with water alone. When a mixture of  $\text{Sb}_2\text{O}_3$  and saturated  $\text{AgNO}_3$  solution was shaken in a quartz vessel under Hg-arc lamps, the oxide turned dark grey. There was no oxygen nor metallic silver produced as occurred when  $\text{CdO}$ ,  $\text{Nb}_2\text{O}_5$ , or  $\text{TiO}_2$  were used in place of  $\text{Sb}_2\text{O}_3$ . Renz represented the change as



He identified antimony metal and  $\text{Sb}_2\text{O}_5$ , but his tests for the latter do not appear to be conclusive. He found a small photo-effect with  $\text{Sb}_2\text{O}_4$  but none with  $\text{Sb}_2\text{O}_5$ . The fact that paints containing antimony white turn yellowish in ultra-violet light was mentioned by van Hoek.<sup>3</sup>

In this paper are described experiments on the conditions for photochemical changes of  $\text{Sb}_2\text{O}_3$  alone and with other substances.

## The Forms of Antimony Oxide used and their Optical Properties.

Antimony oxide exists in two modifications, an orthorhombic form, valentinite, and a cubic form, senarmontite, the latter being the stable form at room temperature (transition point  $573^\circ$ ). Valentinite crystals are built up of chains of molecules and have free valencies on their ends, while senarmontite crystals are built of closed  $\text{Sb}_4\text{O}_6$  units arranged in a face-centred lattice. Valentinite is the more chemically active form and Cagliotti and Milazzo<sup>4</sup> have offered an explanation on crystallographic grounds. The preparation of both senarmontite and valentinite by precipitation is described by Serra,<sup>5</sup> by Bloom and Buerger<sup>6</sup> and by Bloom.<sup>7</sup> It is, however, at present impossible from the method of preparation to be certain of the structure of the substance obtained, and, therefore, all specimens used here have been controlled by taking Debye-Scherrer patterns.

It has long been known that antimony oxide absorbs in the ultra-violet<sup>3</sup> and the reflection curve of one sample has been measured.<sup>8</sup>

<sup>1</sup> C. Renz, *Helv. chim. Acta*, 1921, 4, 961.

<sup>2</sup> *Ibid.*, 1932, 15, 1077.

<sup>3</sup> C. P. van Hoek, *Farben Zeitung*, 1932, 37, 1222, and 1255.

<sup>4</sup> V. Cagliotti and G. Milazzo, *Ric. sci. Progr. tech. Econ. naz.*, 1938, 9, II, 358; *Zentralblatt*, 1939, 1, 3598.

<sup>5</sup> A. Serra, *Z. Kristallogr.*, 1935, 91, 371.

<sup>6</sup> M. C. Bloom and M. J. Buerger, *ibid.*, 1937, 96, 365.

<sup>7</sup> M. C. Bloom, *Am. Mineralogist*, 1939, 24, 281.

<sup>8</sup> C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 902.

Billy and Berton<sup>9, 10</sup> made semi-quantitative studies of the two forms but give no details of their materials. The absorption spectrum of all samples used here has been determined by the diffuse reflection method.<sup>11</sup> Comparisons were made with MgO which reflects 97 %<sup>12</sup> at all wave-lengths used, *i.e.*, from 550  $m\mu$  to 230  $m\mu$ .

**Valentinite—samples  $Sb_2O_3$  (pr.), and  $Sb_2O_3$  (H. and W.).**

A sample,  $Sb_2O_3$  (pr.), was prepared by adding crushed crystals of pure  $SbCl_3$  to boiling aqueous ammonia, washing until free from  $Cl^-$  and drying in a desiccator (first over  $CaCl_2$  under vacuum, then over  $P_2O_5$ ). The powder was a clear white. The Debye-Scherrer pattern was identical with a pattern taken with natural valentinite, which pattern is easily distinguishable from that of senarmontite.<sup>6</sup>

The diffuse reflection of  $Sb_2O_3$  (pr.) falls rapidly at about 385  $m\mu$  (see curve I in the Fig.) indicating that strong absorption sets in at this wave-length. The diffuse reflection spectrum of powdered natural valentinite is also shown (curve II) and it is seen that it is near to that of  $Sb_2O_3$  (pr.).

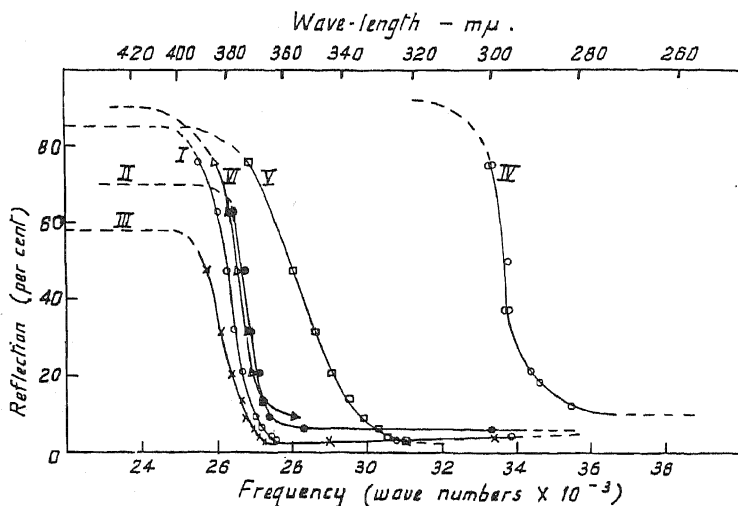


FIG. 1.—The Reflection spectra of different samples of antimony oxide. Curve I—(pr.) and (H. and W.), II—natural valentinite, III—(H. and W.) heated to 400°, IV—Senarmontite (sub.), V—(hyd.) I, VI—(hyd.) III.

The transmission spectrum of a thin flake of natural valentinite 0.02 mm. thick showed a sharp threshold at about 365  $m\mu$ , the absorption at this wave-length being about 75 %. Thicker flakes showed absorption at slightly longer wave-lengths, but as they were not clear, no quantitative measurements could be made. The spectrum of the light reflected from the flake was found to have a marked depression in intensity, beginning at 368  $m\mu$  with a rise to almost the original value at 360  $m\mu$ . This is probably due to the fact that at wave-lengths longer than 368  $m\mu$  reflection comes from both surfaces, while absorption below this wave-length reduces the reflection from the back surface. The subsequent rise may be due to an increase in refractive index associated with the increase in absorption and hence increased reflection from the front surface. Billy and Berton<sup>9</sup>

<sup>9</sup> M. Billy and A. Berton, *Comptes rendus*, 1938, 206, 1631, 1958.

<sup>10</sup> A. Berton, *ibid.*, 1938, 207, 625.

<sup>11</sup> See, for example, C. F. Goodeve, *Trans. Faraday Soc.*, 1937, 33, 340.

<sup>12</sup> J. Preston, *Trans. Opt. Soc.*, London, 1930, 31, 15; and Taylor, *J. Opt. Soc. Am.*, 1934, 24, 192.

found a minimum in the diffuse reflection of powdered valentinite at  $362\text{ m}\mu$  followed by a rise to a maximum at  $355\text{ m}\mu$ . They attributed the rise to a decrease in absorption, but it is more likely that it is due to the same cause as above, *i.e.*, increased reflection on front surfaces. Microphotometer curves of our spectrum plates for powdered valentinite did not show such a rise but only a slight inflexion at about  $360\text{ m}\mu$ .

The sample  $\text{Sb}_2\text{O}_3$  (H. and W.), was commercially pure and supplied by Hopkin and Williams. It was a fine powder with a faint brownish yellow tint which disappeared when the powder was stored in the dark over  $\text{P}_2\text{O}_5$ , but not when in contact with the atmosphere. The Debye-Scherrer pattern and the reflection spectrum were identical in every respect with those of  $\text{Sb}_2\text{O}_3$  (pr.), showing that the substance was valentinite.

Both samples contained water (perhaps also traces of excess oxygen). Simon and Poehlmann<sup>13</sup> have shown that there exist no hydrates of  $\text{Sb}_2\text{O}_3$ . Water accordingly could be removed by storing over  $\text{P}_2\text{O}_5$ , although only very slowly; after eight months' drying there was still water in the samples. The water was given off rapidly when the substances were heated in vacuum, the bulk of the water coming off at about  $250^\circ$ . Two samples of (H. and W.) kept in vacuum for two hours at about  $350^\circ$  and  $400^\circ$  respectively turned a little greyish, but the Debye-Scherrer patterns and the threshold of absorption (see Curve III) were unchanged, showing that, even with this treatment, the valentinite had not changed into the stable modification. (In order to compare Curve III with Curve I the former should be multiplied by 1.45, *i.e.*, the ratio of the reflections in the visible.) Samples of  $\text{Sb}_2\text{O}_3$  (pr.) and of  $\text{Sb}_2\text{O}_3$  (H. and W.) dried over  $\text{P}_2\text{O}_5$  for  $2\frac{1}{2}$  months at room temperature gave by titration with  $\text{KBrO}_3$  99.4 % and 98.6 %  $\text{Sb}_2\text{O}_3$  respectively, indicating a higher water content of the latter. No change in the reflection spectra could be detected after 8 months' drying.

#### Senarmontite—sample $\text{Sb}_2\text{O}_3$ (sub.).

Clear colourless crystals of pure senarmontite were prepared by sublimation of  $\text{Sb}_2\text{O}_3$  (H. and W.) at  $400^\circ$  to  $500^\circ$  and at  $10^{-2}$  mm. pressure. The crystals which were octahedral, of sizes up to 1 mm., were generally crushed before use. Their Debye-Scherrer pattern was identical with that shown for senarmontite.<sup>6</sup> The threshold of absorption was found at  $300\text{ m}\mu$  (see curve IV) in agreement with the observation of Billy and Berton.<sup>9</sup> This means that the principal absorption band of the senarmontite unit,  $\text{Sb}_4\text{O}_{10}$ , begins at about this wave-length. The diffusely reflected light from the unpowdered crystals, however, showed the presence of absorption up to  $340\text{ m}\mu$ . The average light path in this case traverses a much thicker layer of crystal, and therefore weaker absorption shows up.

#### Samples prepared by Hydrolysis, $\text{Sb}_2\text{O}_3$ (hyd.).

Bloom<sup>7</sup> found that the products obtained by hydrolysis of antimony salts which had been dissolved in the respective acids depended upon the concentration of the free acid, higher concentrations favouring valentinite. Certain mixed forms were described by Bloom and Buerger.<sup>8</sup>

A sample,  $\text{Sb}_2\text{O}_3$  (hyd.) I, prepared by dissolving  $\text{SbCl}_3$  in  $\text{HCl}$ , neutralising the excess with  $\text{Na}_2\text{CO}_3$  and adding drop by drop to a large excess of boiling water, showed only very few and rather diffuse Debye-Scherrer lines that suggested that the substance was senarmontite. Its reflection spectrum is shown by Curve V, and while it does not agree with that of senarmontite the difference could be accounted for if we assume that there is only a trace of valentinite present. It is probably a transition form.

On the other hand, slight alterations in the procedure gave different results. Solution of  $\text{SbCl}_3$  in  $\text{HCl}$ , addition of cold water until a precipitate just formed, filtration and addition of the clear filtrate to boiling water

<sup>13</sup> A. Simon and H. Poehlmann, *Z. anorg. Chemie*, 1925, 149, 101.

which was kept boiling for 90 minutes, gave a well-crystalline product (hyd.) II, whose pattern and spectrum were identical with those of valentinite. A sample prepared by addition of  $\text{SbCl}_3$  crystals directly to cold water and washing by decantation with boiling water gave a product (e.g., sample (hyd.) III) whose pattern, while indicating that it was well crystallised, was quite different from that of either senarmontite or valentinite. Neither the pattern nor the crystal shape was entirely reproducible. The reflection spectrum of (hyd.) III, Curve VI, was almost identical with that of powdered valentinite.

These results do not easily fit in with those of Serra <sup>5</sup> or of Bloom and Buerger <sup>6</sup> although they are nowhere in direct conflict. In agreement with the latter authors we found it impossible to remove all of the chloride from samples prepared by hydrolysis. Considerably more systematic work would be necessary before the conditions could be standardised to produce a given form. The importance of this preliminary work lies in the fact that the photosensitivity of antimony oxide prepared by hydrolysis has been shown to be considerably less than that of other crystalline forms (see Obs. 6 and 20, below). It appears that the reflection spectrum is not sensitive to all changes in crystal form (*cf.* Billy and Berton <sup>9</sup>).

### The Darkening of Antimony Oxide by Light.

Samples of the above preparations were exposed to the full light of the mercury arc (usually a Hanovia low pressure type) in the open or in flat quartz illuminating vessels at a distance of about 15 cm. Most of the observations have been repeated several times.

The results are summarised as follows :—

(1)  $\text{Sb}_2\text{O}_3$  (H. and W.) showed visible yellowing in 5 seconds, turning to light brown in 30 minutes. There was practically no further change up to several hours.

(2) The efficiency of darkening was independent of light intensity—an exposure four times as long with light four times as weak gave an identical darkening.

(3) The rate was unchanged by addition of liquid water. After five hours' illumination of a stirred mixture, a test for  $\text{H}_2\text{O}_2$  with  $\text{Ti}(\text{SO}_4)_2$  was negative.

(4)  $\text{Sb}_2\text{O}_3$  (pr.) behaved as in (1) except that it was slower.

(5) Valentinite (natural) and senarmontite ( $\text{Sb}_2\text{O}_3$  sub.) were not sensitive to irradiation. The latter showed no visible colouring after 5 hours' exposure. It is therefore at least 2000 times less sensitive than (H. and W.). Addition of water did not induce sensitivity.

(6) All samples of  $\text{Sb}_2\text{O}_3$  (hyd.) were found to be insensitive either in the presence or absence of water.

(7) Drying of  $\text{Sb}_2\text{O}_3$  (H. and W.) over  $\text{P}_2\text{O}_5$  for a few days produced no change in sensitivity, but after 6 months the illumination necessary to produce noticeable darkening was 100 times longer than that for an undried blank. The final degree of darkening was also much less.

(8) Drying  $\text{Sb}_2\text{O}_3$  (H. and W.) by baking for half an hour at  $350^\circ$  in a vacuum rendered it completely insensitive. Addition of water did not restore any sensitivity in 8 hours, but on keeping in the atmosphere for 14 days a slight sensitivity was found.

(9) (H. and W.) which was irradiated under vacuum in the cold darkened at the same rate as in observation (1). On heating the *darkened* sample under vacuum to  $250^\circ$  it quickly faded to its original white. This temperature coincides with that at which there is a rapid loss of water.

(10) A sample (H. and W.) thoroughly darkened as in (9) did not fade appreciably after 12 months in air over  $\text{P}_2\text{O}_5$  in the dark.

(11) Extensive attempts were made with (H. and W.) and (pr.) to test whether oxygen was evolved in the photochemical change. A highly

evacuated quartz vessel,  $8 \times 1.5 \times 0.3$  cm., containing the sample, was connected to a capillary discharge tube, the spectrum of which could be examined by means of a Hilger quartz Raman spectrograph, exposure 10 to 60 sec. It was impossible to obtain completely conclusive results owing to the adsorbed water (and possibly oxygen) which was evolved by illumination in the cold (due to heating by the light from the arc, even when filtered from infra-red). The water dissociated in the discharge and gave the oxygen spectrum. If it was removed by heating to  $350^\circ$  the powder became insensitive, but a partially effective compromise was obtained by heating to  $100^\circ$  in vacuum for one hour. Subsequent illumination in the cold gave darkening but no gas evolution. In one experiment illumination for 8 hours gave a darkening which should have produced a pressure of oxygen at least of the order of 10 mm. (assuming the maximum possible extinction coefficient,  $10^{-16}$  cm.<sup>2</sup>, for the dark substance). The accuracy of the tests was sufficient to show that the oxygen pressure could not have been anything like as high as this. It is therefore to be concluded that no appreciable free oxygen is evolved in the photochemical darkening process.

### Wavelength Considerations.

Preliminary experiments with filters confirmed the expectation that the darkening described above occurred with ultra-violet and not with visible or infra-red light. Later, the threshold of photosensitivity was accurately determined simply by exposing a glass plate covered with the powder in the high-aperture Raman spectrograph. The powder  $\text{Sb}_2\text{O}_3$  (H. and W.) was made into a thin paste with water, painted on to the glass plate and dried in the dark in a desiccator. Exposures to a pointolite lamp of various times from 5 to 20 hours showed that a very sharp threshold of darkening occurred at  $375 \text{ m}\mu$ . Its position was unchanged by the presence of glycerol (see obs. 13). The agreement between this threshold and that of absorption (see Fig.) is satisfactory and indicates that the substance giving rise to this absorption is responsible for initiating the photochemical process (glycerol does not absorb except in the far u.v.).

Using a Hg-arc lamp, a series of exposures on  $\text{Sb}_2\text{O}_3$  (H. and W.) were compared with a similar series on an ordinary AgBr photographic plate (at, of course, an enormously reduced range of exposures) and showed that from  $365 \text{ m}\mu$  to below  $240 \text{ m}\mu$  the sensitivity of  $\text{Sb}_2\text{O}_3$  was parallel to that of AgBr. As the photosensitivity of the latter is almost independent of wave-length over this range<sup>14</sup> we can conclude that that of  $\text{Sb}_2\text{O}_3$  is also independent of wave-length.

### The Photo-Darkening of Antimony Oxide in the presence of other Reagents.

For the tests summarised below the powder was placed in the cavities of a porcelain test plate and sufficient liquid or solution added just to cover it. The whole was covered by a quartz plate, cooled by an air stream and illuminated with a Hg-arc as before. All results have been repeated at least twice and there were full comparison blanks to test the absence of thermal effects, etc.

(12) The rate of darkening of  $\text{Sb}_2\text{O}_3$  (H. and W.) is uninfluenced by added water, butyl or amyl alcohol, formaldehyde or linseed oil varnish.  $\text{Sb}_2\text{O}_3$  (sub.) remained insensitive in the presence of these reagents.

(13) The rate of darkening of (H. and W.) and (pr.) was increased by the addition of glycerol (commercial or "Analar") and the final degree of darkening was a deep black, much stronger than that obtained with the dry powder (*cf.* obs. 1). This final state was attained in about 40 minutes. There was also an increase with ethylene glycol and sugar solutions.

<sup>14</sup> Private communication from Dr. E. S. Sheppard, Eastman Kodak Co., Ltd.

(14)  $\text{Sb}_2\text{O}_3$  (sub.) in the presence of glycerol darkened at a *faster* rate than did (H. and W.) in obs. 13. A filter cutting out all light below  $330\text{ m}\mu$  stopped the reaction entirely. (Compare absorption of senar-montite.) The presence of 25 % of water in the glycerol had no effect, but with 50 % the reaction practically ceased (*cf.* obs. 16).

(15) Natural valentinite darkened with glycerol.

(16)  $\text{Sb}_2\text{O}_3$  (sub.) which had been darkened as in obs. 14, returned to its original white when left in the room for about a day. The cycle was repeated several times on the one sample. If left in dried air or in pure water vapour at room temperature the reversal was very much retarded. Addition of liquid water or methyl or ethyl alcohol to samples darkened as in obs. 14 caused an almost immediate reversal. Acetone, which is not soluble in glycerol, caused no effect.

(17)  $\text{Sb}_2\text{O}_3$  (H. and W.) or (pr.), darkened as in obs. 13, did not whiten again but returned to that brownish shade which would have been obtained by irradiating the powder alone.

(18) Hydroxylamine hydrochloride, hydrazine hydrate and sulphate and KI solutions all gave higher rates than in obs. 13, and the darkening was *irreversible*. With the nitrogen compounds gas was evolved. There was no thermal reaction even at  $100^\circ$ .  $\text{Sb}_2\text{O}_3$  (sub.) with these substances darkened at a slightly lower rate, presumably due to the fact that it absorbs only the further ultra-violet.

(19) The brown powders of obs. 1 and 3 and the black powders of obs. 13 and 14 were completely soluble in HCl, giving colourless solutions. The black powder of obs. 18, however, left a residue of black particles. Antimony metal, having a normal potential with respect to hydrogen of approximately  $+0.2$  volts<sup>15</sup> should be insoluble in acids, but may become soluble due to the small size of the particles in obs. 1, 3, 13 and 14, and to the presence of oxygen. The black residue from obs. 18 consists, presumably, of larger particles of antimony metal. The solubilities in HCl are parallel to the observations of the reversibility of the darkening; samples showing reversal being soluble, the others not.

(20) Samples of  $\text{Sb}_2\text{O}_3$  (hyd.) in contact with glycerol darkened at a lower rate and to a lower final extent than any other preparation; (hyd.) III was less sensitive than (hyd.) I or II.

(21)  $\text{Sb}_2\text{O}_3$  (H. and W.) is also able to act as a photosensitiser in a way similar to  $\text{TiO}_2$ .<sup>8</sup> Dyes such as methylene blue, chlorazol orange POS and chlorazol sky blue FF were readily decolorised when adsorbed on  $\text{Sb}_2\text{O}_3$  and exposed to a Hg-arc; whereas comparison samples adsorbed on  $\text{BaSO}_4$  were unchanged.<sup>16</sup> There was no obvious darkening of the  $\text{Sb}_2\text{O}_3$ .

### Conclusions.

In any photosensitive system there must be present a light absorbing species and a potentially-reactive centre. If these are separated, it is necessary to postulate a mechanism by means of which the energy of the quantum may be transferred as a more or less complete unit, an "exciton" from the point of absorption to the centre. Two such mechanisms have recently been discussed.<sup>8,17</sup> The success of the transference of the energy of the quantum to the potentially reactive centre depends upon the competition with the process of degradation of this energy to heat, or with fluorescence. None of the samples, however, showed fluorescence.

In all observations recorded above (with the exception of obs. 18) it has been shown that the absorption was associated with the antimony

<sup>15</sup> Landolt-Bornstein II. *Ergbol.*, p. 971.

<sup>16</sup> J. A. Kitchener, *Unpublished Experiments*.

<sup>17</sup> C. F. Goodeve, *Nature*, 1939, **143**, 1007.

oxide, but that the threshold of absorption depends upon the arrangement of the atoms. There is no possibility of the absorption being due to irregularities in the crystal lattice as suggested by Gurney<sup>18</sup> for ZnS, as the precipitated powders give the same absorption as the pure crystals.

The conditions for sensitivity to light, which are presumably determined by the potentially-reactive centre, are concerned with both the crystal lattice and the presence of some second species, either water (obs. 7 and 8) or certain reducing agents (obs. 13-20). The mechanisms, however, of the processes with water and with the other substances are apparently different, and are therefore to be considered separately.

The photochemical change with water might be called an *internal* process. The water must be "built in" to the crystal lattice in a special manner (*cf.* obs. 7 and 8 with 3); it cannot enter completed valentinite or senarmontite lattices. It apparently can re-enter slowly a valentinite lattice from which it has been removed (obs. 8). The photochemical process appears to be a reduction of antimony oxide to the metal, the oxygen being retained in a neighbouring position. This would account for the reversal of the darkening and for the absence of evolved oxygen (obs. 11). It is possible that water acts by distorting the lattice, thus facilitating the photodecomposition and then stabilises the new chemical arrangement; otherwise the antimony, which is so finely divided that it dissolves in HCl, would be re-oxidised immediately on contact with air (*cf.* obs. 16). That the stabilisation is fairly complete is shown by the fact that the reversal of the process takes place appreciably only on the removal of water by heating (obs. 9). It is of interest to point out that zinc sulphide, which blackens with light in the presence of water, shows a reverse reaction at room temperature.<sup>19</sup> Reactive centres of valentinite with water are independent of those formed with glycerol (obs. 17). The "internal darkening" does not cease because of protection against the radiation by absorption by the products, but rather when all of the potentially reactive centres have been used up (obs. 1 and 7).

The "external" photochemical reduction of  $\text{Sb}_2\text{O}_3$  by reducing agents is of especial interest. Their activity is highly specific and does not depend only on their ordinary reducing power (*cf.* obs. 12 and 13-19). With strong reducing agents, such as  $\text{N}_2\text{H}_4$  or  $\text{NH}_2\text{OH}$ , all  $\text{Sb}_2\text{O}_3$  centres, including those with water, are attacked photochemically with the formation of Sb metal. The reduction is irreversible and the metal does not dissolve in HCl. With glycerol the reaction is reversed, presumably when the protective action of the glycerol is destroyed. This apparently occurs when the viscosity is lowered and oxygen can be taken up more rapidly. As the metallic reduction product dissolves in HCl, it is to be concluded that it is in a finely divided state.

All reactive centres containing  $\text{Sb}_2\text{O}_3$  (hyd.) were the least sensitive of any, a fact which may be of practical importance. This low sensitivity might be attributed either to the chloride present or to a strong tendency for degradation of electronic energy to heat in such irregular lattice structures (see Frenkel<sup>20</sup>). The effect is parallel to the inhibiting action of adsorbed sulphate on  $\text{TiO}_2$ .<sup>21</sup>

<sup>18</sup> R. W. Gurney, *Trans. Faraday Soc.*, 1939, **35**, 98 and 143.

<sup>19</sup> N. T. Gordon, F. Seitz and F. Quinlan, *J. Chem. Physics*, 1939, **7**, 4.

<sup>20</sup> J. Frenkel, *Physik. Z. Sow.*, 1936, **9**, 158.

<sup>21</sup> C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, **34**, 572.



The authors are indebted to Dr. J. A. Kitchener and Mr. M. R. Taylor for their kind assistance, and to Mr. F. A. Bannister of the British Museum, Department of Mineralogy, for the provision of samples of valentinite.

### Summary.

The photochemical sensitivity and the absorption spectra of the different crystalline forms or states of  $\text{Sb}_2\text{O}_3$  have been investigated. All forms are sensitive to irradiation only when some foreign substance is present. There are two different types of photoreaction, both apparently with formation of antimony metal. The orthorhombic form of  $\text{Sb}_2\text{O}_3$  is able to "build in" water forming an internal photoactive system. The reaction is reversed by removal of the water. With certain reducing agents an external photodecomposition occurs with all forms of  $\text{Sb}_2\text{O}_3$ . Little or no sensitivity was shown by samples prepared by hydrolysing  $\text{SbCl}_3$  with water. With glycerol the reaction is reversed if oxygen together with water or other liquid miscible with glycerol are taken up.

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## DIELECTRIC LOSS IN POLYSTYRENE MIXTURES.

BY F. C. FRANK AND WILLIS JACKSON.

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During recent years a number of investigators have sought to clarify the mechanisms underlying the energy loss which occurs in dielectrics when they are subjected to alternating electric fields. In this connection the authors have previously studied the behaviour of paraffin waxes containing small percentages of known polar "impurities" and endeavoured to correlate the experimental results obtained with the dipole theory of Debye.<sup>1,2</sup>

This theory predicts that the dielectric loss due to a polar constituent present in a non-polar dielectric medium will pass through a maximum with variation either of the temperature or of the frequency of the applied electric field, and relates the height of this maximum to the dipole moment and concentration of this polar constituent. The concentration is assumed to be sufficiently small to ensure the absence of interaction between individual polar molecules, and in the paraffin wax solutions referred to, where this condition was satisfied, the quantitative agreement between the observed and calculated loss maximum was good, in spite of the fact that the physical concepts on which the original theory is based seem quite unsuited to the solid state.

The theory also relates the position of the dielectric loss maximum in the spectra of frequency and temperature to the size of the orienting

<sup>1</sup> W. Jackson, *Proc. Roy. Soc. A.* (1935), **150**, 197.

<sup>2</sup> F. C. Frank, *Trans. Faraday Soc.* (1936), **32**, 1634.

polar group and the viscosity of the environment in which it is situated, and the uncertainty attaching to the applicability of the theory in the above case was emphasised when on calculation it was found that the "apparent viscosity" of the solid paraffin wax medium at room temperature to the orientation within it of polar molecules of similar structure was less than 10 poise.

By way of extending the scope of the measurements into a range of materials considerably harder than paraffin wax, it was decided to investigate the possibility of using polystyrene. This substance, which as a hydrocarbon is practically free from dielectric loss over the whole of the frequency range from 50 to  $10^6$  cycles per second, is available commercially as a thermo-plastic moulding material under the name of Trolitul. The practical problem was to prepare plates of this substance, containing small percentages of various substances, whose effect on the dielectric properties could be anticipated from the dipole theory, of a size (6 in. diam.  $\times$   $\frac{1}{16}$  in. thick) and quality suitable for the dielectric measurements.

### Preparation of the Test Specimens.

At the preliminary stage a number of specimens were prepared from a granulated form of the material in the I.C.I. research laboratories, employing the normal high-pressure moulding technique. Lower temperatures and longer moulding times were used than in the method finally adopted, and some of the samples (*e.g.* those containing small percentages of benzoic acid and *p*-toluidine) caused great difficulty by sticking to the moulds. The added substances also crystallised out from mixtures of a concentration which gave perfectly clear mouldings by the subsequent low-pressure method. The surface of the plates was unsatisfactory and the specimens showed appreciable distortion, which became very marked on heating to the softening temperature.

In the low pressure method developed in the laboratory the major difficulty was that of removing air bubbles without reaching temperatures productive of depolymerisation and oxidation. The various polar materials added to the polystyrene acted to some extent as plasticisers and assisted in this process, but it was sometimes necessary to add a little naphthalene also.

The technique finally adopted was as follows: The mixture was placed in an enamel dish, covered with a clock glass and clamped rigidly in an oil bath, and heated to a temperature at which easy stirring became possible. This temperature was usually between 200 and 250° C., but was kept as low as possible so as to reduce fuming, oxidation and boiling out of the added substance during the mixing process. The mixture was alternately stirred and left to stand at this temperature and then taken up to about 290° C. for a short time to free it from bubbles. It was then cooled to about 260° C., which was found to be a convenient temperature for pouring.

The mixture was poured on to a hot flat plate of brass and pressed into shape with another similar plate fitted with a lifting handle, and with three set-screws at its edge to determine the thickness of the final specimen. A thin film of vaseline rubbed over the plates ensured that they could be lifted away from the specimen on cooling to room temperature, although cooling with ice was occasionally necessary.

Satisfactory mouldings were produced of the following mixtures:—

- (a) 17.5 % butyl phthalate.
- (b) 16.3 % chlorinated diphenyl. ("Permitol"—a mixture approximating to tetrachlorodiphenyl.)
- (c) 7.95 %  $\beta$ -naphthol + 3.5 % naphthalene.
- (d) 12.8 %  $\beta$ -naphthol.
- (e) 4.8 % cetyl palmitate + 2.3 % naphthalene.

### The Dielectric Loss Measurements.

The measurements consisted of a study of the variation of the dielectric loss factor— $\tan \delta$ —with temperature at convenient frequencies in the range  $10^6$ – $10^7$  cycles per second. The method employed was a resonance substitution one, the circuit diagram for which is shown in Fig. 1. In order to avoid any assumption regarding zero loss in the comparison air condenser, and at the same time to allow for any residual loss in the test

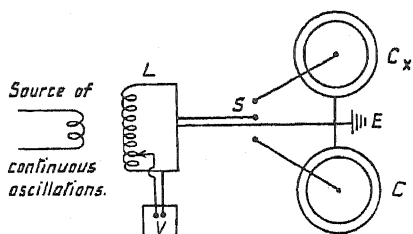


FIG. 1.

$C_x$ —test condenser,  
 $C$ —identical air condenser,  
 $S$ —change-over switch,  
 $E$ —earth point,  
 $V$ —thermionic voltmeter.

condenser not arising from the inserted dielectric, use was made of two condensers  $C$  and  $C_x$  of identical construction. A description of these condensers and of the arrangement for their temperature variation has been given elsewhere.<sup>1</sup> The dielectric to be investigated was placed in  $C_x$  and the capacitance of  $C$ , having air dielectric, was then adjusted until it equalled that of  $C_x$ . When this adjustment had been made the circuit remained in resonance to the frequency of measurement when the condenser was changed from  $C_x$  to  $C$  at the switch  $S$ . The loss factor of the

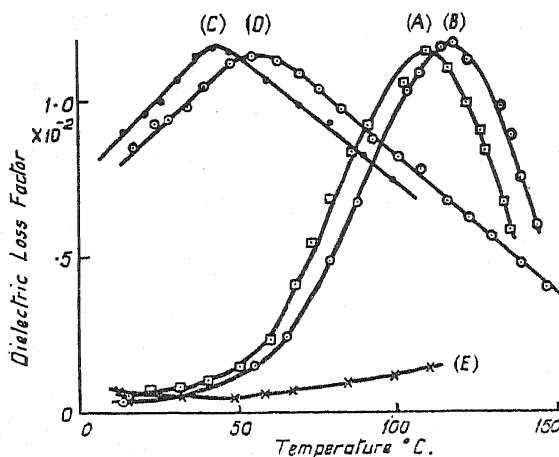


FIG. 2.

Curves (A) and (B)—  
 Chlorinated diphenyl  
 mixture.

(A)— $10^6$  cycles,  
 (B)— $4.8 \times 10^6$  cycles  
 per sec.

Curves (C) and (D)—  
 Butyl phthalate  
 mixture.

(C)— $0.82 \times 10^6$  cycles,  
 (D)— $7.5 \times 10^6$  cycles  
 per sec.

Curve (E)—Cetyl pal-  
 mitate mixture.

Frequency  $5 \times 10^6$   
 cycles per sec.

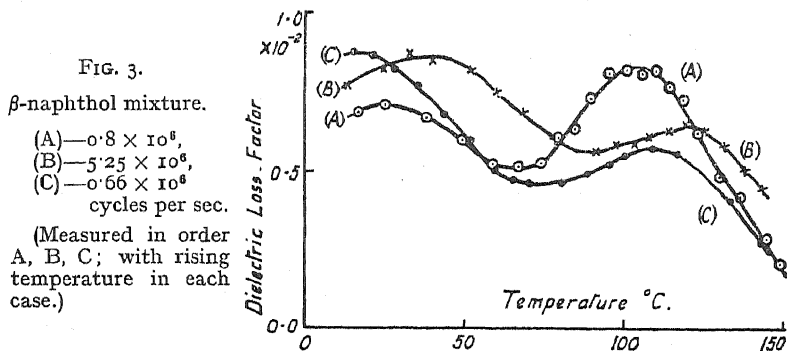
dielectric of  $C_x$  was derived from the difference between the total circuit loss when the capacitance was formed by  $C_x$  and by  $C$ . The loss in each case was deduced from the width of the resonance curve delineated on the thermionic voltmeter by suitable incremental changes in the oscillator frequency about the resonant value.

The experimental results on the moulding mixtures previously referred to are given in Figs. 2 and 3.

### Discussion.

The results demonstrate that the hard polystyrene environment imposes no very severe restriction on the orientation within it of polar

molecules of the type considered. The curves (A) and (B), Fig. 2, relating to the moulding containing *chlorinated diphenyl* are of particular interest in view of the fact that the behaviour of this material in bulk has been studied by one of the authors.<sup>3</sup> At a frequency of  $0.95 \times 10^6$  cycles, closely that to which curve (A) relates, the chlorinated diphenyl alone gave a very sharp loss maximum at a temperature of  $26^\circ \text{C}$ . when the material was a liquid of viscosity coefficient about 100 poise. The polystyrene environment has had the effect of shifting the position of the loss maximum to  $110^\circ \text{C}$ ., and further of broadening the loss—temperature curve—reckoned at half its height—from  $13^\circ \text{C}$ . to  $60^\circ \text{C}$ . These curves (A) and (B) are indeed very much broader than the theoretical form, and this is no doubt to be accounted for on the grounds that the complicated structure of the polystyrene glass provides a wide range of different environments for the orienting polar molecules. The absence of appreciable dielectric loss at  $26^\circ \text{C}$ . suggests that the chlor-



inated diphenyl molecules are not clustered to any very considerable extent.

The *butyl phthalate* curves (C) and (D), Fig. 2, are extraordinarily broad, although this is perhaps to be expected, because besides polarisation by rotation of the molecule as a whole parts of it can move in several different ways. Even so the spread is surprising, indicating the presence of polar groups operating under a range of restriction varying by a factor of some millions. The behaviour is probably bound up with the very strong solvent action of the butyl phthalate, this particular moulding softening at relatively low temperatures.

The effect of the addition of *cetyl palmitate*, the solute employed in the paraffin wax work previously referred to, is small (curve E, Fig. 2), the steady rise in  $\tan \delta$  from  $50^\circ \text{C}$ . upwards possibly forming part of a broad absorption curve the maximum of which was not reached. In an effort to locate such a maximum for comparison with the results of the paraffin wax work, measurements were made also at 50 cycles using a Schering Bridge but unfortunately without success.

The *β-naphthol* mixtures were studied to test the hypothesis that rotation of the hydroxyl group by itself is responsible for dielectric loss in such substances as bakelite. As anticipated, the results showed two loss maxima in the temperature curve, Fig. 3, corresponding to

<sup>3</sup> W. Jackson, *Proc. Roy. Soc. A* (1935), **153**, 158.

the two clearly defined modes of dipole orientation which can occur in this molecule, one, the lower temperature one, due to rotation of the hydroxyl group by itself, and the other to rotation of the molecule as a whole. A comparison of curves (A), (B), and (C), all relating to the same sample and obtained in this order, however, shows that the behaviour is more complex than this. In the specimen as first prepared the low temperature maximum is smaller, and the high temperature maximum larger, than after the "annealing" which takes place during measurement. By way of explanation, it may be suggested that in any viscous medium any equilibrium which depends upon temperature is liable to become "frozen-in" at the lower temperature, a condition which can be partially removed by annealing. Here we have such an equilibrium in the strong tendency of hydroxyl groups to associate with one another, and in the consequent molecular clustering. It may reasonably be surmised that this is the cause of the annealing effects, though it is not easy to explain them in detail, for first considerations lead one to expect rather the reverse of what is observed. Until further work has clarified the point, the explanation given above for the two maxima must therefore remain a working hypothesis, for all that the explanation preceded the discovery.

Conductivity measurements on this  $\beta$ -naphthol sample showed that ionic conduction was not a significant factor affecting the dielectric loss measurements.

It is of interest to consider these results in relation to dielectric materials of technical importance. It is clear from the behaviour of the chlorinated diphenyl moulding that the motion of large rigid molecules, of which chlorinated diphenyl is an example, can be effectively prevented at normal temperatures, such that in spite of their presence in appreciable concentration the loss factor can become less than  $5 \times 10^{-4}$ . Even so, in view of the loose places which are not to be avoided in a glass-like system, it is improbable that any plastic having markedly polar groups in it can reach the highest class of loss-free dielectrics. With materials such as bakelite, however, the chance of freezing-out polar orientation is much more remote, for even if the benzene nucleus is firmly tied down by covalencies, the hydroxyl groups will still be able to orient independently.

All organic solids with useful strength are composed of at least one-dimensionally giant molecules; and all may be regarded as composed of one-dimensional polymers cohering in various ways. Firstly, are long molecules cohering only by weak van der Waals' forces, *e.g.* reduced rubber (an aliphatic hydrocarbon), ordinary rubber containing double bonds, and polystyrene containing phenyl groups, the two groupings of which successively increase the adhesion by increasing the polarisability though without introducing appreciable polarity. The solids which these form are rather weak; moreover their cohesion can be overcome by thermal agitation at moderate temperatures, passing first through an elastic stage (in which rubber finds itself at room temperature) to a plastic stage before reaching the decomposition temperature, above 200° or so, at which covalencies are rapidly broken. One may say with reasonable certainty that no such material can be expected to retain its rigidity above 120°, the approximate asymptotic melting-point of all aliphatic homologous series.

Next, are the long molecules containing oxygen, nitrogen or halogens (*e.g.* polyesters or chlorinated rubber) where the cohesion is enhanced

both with the polarity and the polarisability. These may have greater strength but they still retain their "thermoplasticity." At a third stage the chains are bound laterally by hydrogen bonds, with increased strength, as in cellulose: heat alone, without a solvent, is no longer sufficient to loosen the chains from one another without at the same time breaking them.

Finally, we have covalent binding between the chains producing three dimensional polymers, in which class the greatest strength is to be found. Since, however, neither heat nor solvent can make such a material plastic it is less easy to bring into a desired form than others. If it is to be moulded, the polymerisation must be completed *in situ*, an intermediate state in the preparation being used as a "thermosetting" plastic (e.g. bakelite, vulcanised rubber). Here, then, arises the difficulty: the intermediate state must contain reactive groups so that the polymerisation can go further, but it is not entirely an accident that practically all reactive groups are polar. The only important exception is the double bond, and that also requires a rather large activation energy unless sensitised by a neighbouring polar group, polymerisation through double bonds being otherwise always a chain-building chain-reaction. This may serve to explain why as yet there is no very strong non-polar plastic. Divinyl benzene produces a brittle incoherent polymer, though a little divinyl benzene may be added to styrene to produce a polymer free from the tendency to swell in organic solvents. Diamond is, of course, the ideal non-polar three-dimensional giant organic molecule, and suffers outstandingly from the typical defects, difficulty of shaping, impossibility of synthesis *in situ*, difficulty of obtaining sufficiently large pieces.

This work was done in the Engineering Science Laboratory at Oxford, and the authors are indebted to the inspiration of Mr. E. B. Moullin.

*The Laboratory of Colloid Science,  
The University,  
Cambridge.*

*The Electro-technical Laboratories,  
The University,  
Manchester.*

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## PROPAGATION OF TEMPERATURE CHANGES THROUGH TEXTILES IN HUMID ATMOSPHERES.

### PART I.—RATE OF ABSORPTION OF WATER VAPOUR BY WOOL FIBRES.

BY G. KING AND A. B. D. CASSIE.

*Received 22nd November, 1939.*

Textile fibres normally used for clothing purposes have two properties that enable them under certain circumstances to influence rate of propagation of temperature change in an important manner.<sup>1</sup> The two

<sup>1</sup> Cassie, Atkins and King, *Nature*, 1939, 143, 163.

properties are the hygroscopic nature of the fibres, and their large surface volume ratio. The first makes possible exchange of water vapour between the fibres and an air-water vapour atmosphere. Absorption and desorption are accompanied by comparatively large evolution and absorption of heat, and if the exchange of water vapour takes place sufficiently rapidly, the resultant heat changes can influence propagation of temperature change to a marked degree. The large surface-volume ratio enables the exchange to occur rapidly enough for this to be true.

Part I of the present publication deals with the large surface-volume ratio of the fibres, and describes experimental work which shows how very rapidly wool fibres come to equilibrium with any change in water vapour conditions. Part II gives the theory of propagation of temperature change, and Part III shows its confirmation by experiment.

### Diffusion of Water Vapour into a Wool Fibre.

The radius of an average wool fibre may be taken as  $10\ \mu$ , or  $10^{-3}\text{ cm.}$ , so that 1 c.c. of wool fibre has a surface area of roughly 2000 sq. cm. This large surface-volume ratio means that even if diffusion determines the time for the fibres to come to equilibrium with changed water vapour conditions, this time will be small. The diffusion constant for water in keratin is not known, but if we assume a value as small as  $10^{-5}\text{ cm.}^2/\text{sec.}$ , the time required for a wool fibre to come within 80 % of its equilibrium value when water vapour conditions are changed, is roughly  $10^{-2}\text{ sec.}$  Thus there seems ample margin for the time interval for water vapour exchange to be small enough to enable heat of absorption to play an important part in rate of propagation of temperature change.

### Heat of Absorption and Pick-up of Water Vapour by Wool Fibres.

Trouton<sup>2</sup> remarked that textile fibres appear to absorb water vapour vigorously. This is consistent with the rough discussion in the previous paragraph; but his remark seems to have been overlooked, and later papers<sup>3</sup> have ascribed various apparent slow rates of absorption and desorption to surface forces. These apparently slow rates are due to diffusion in the surrounding atmosphere and to the effect of heat of absorption on the absorption itself. The present paper describes an attempt to measure the rate of absorption of water vapour by the fibres when the complicating influences of diffusion and heat of absorption are eliminated, or allowed for. The results show that slow rates of absorption by textiles are entirely due to external factors and have no relation to the surface structure of the colloids.

### Experimental.

Diffusion of water vapour through any surrounding atmosphere was eliminated by making the experiments *in vacuo*. The general layout is shown in Fig. 1. The wool sample under investigation, W, is suspended from a spiral spring A. The extension of this spring measures the weight of water absorbed by the wool. Other factors that must be measured are the temperature of the wool and the water vapour pressure in the apparatus; the first is measured by a length of fine platinum wire wound

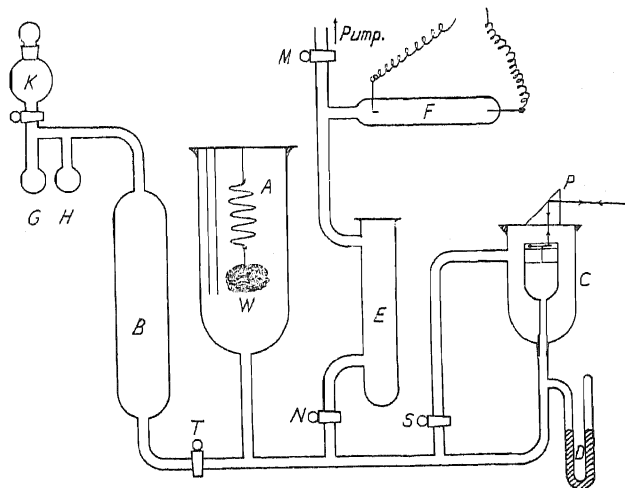
<sup>2</sup> Trouton, *Proc. Roy. Soc., A*, 1906, 77, 292.

<sup>3</sup> Fisher, *ibid.*, 1923, 103, 139.

in with the wool, and the second by the diaphragm manometer C and U-tube D.

Distilled water which had recently been boiled was introduced through the dropping funnel K. A few c.c. were run into G, and remaining air was removed by freezing the water and pumping out the system. The water was then distilled into H to remove last traces of air. B acts as a reservoir for water vapour. It has a capacity of 2 litres and holds enough water

FIG. 1.



vapour to give the wool sample a water content of 10 %. This reservoir prevents cooling effects due to evaporation of water from H on opening T from causing a marked variation in water vapour pressure. Actually, it was found that on opening T the vapour pressure rose to 23.5 mm., the saturation pressure at the thermostat temperature of 25° C., and remained constant at this value.

The sample consisted of about 0.25 gm. of Australian merino wool sliver,

the average fibre diameter being 21  $\mu$ . Grease was removed by treatment in a soxhlet apparatus. It was intimately intertwined with about 16 cm. of No. 50 S.W.G. platinum wire, and wound into a loose bundle with roughly 0.5 cm. of each end of the wire exposed. This bundle was attached to the spiral spring A, the extension of which was measured by a travelling microscope.

The platinum wire and its leads formed one arm of a Wheatstone bridge. The other arms were of manganin wire each of resistance approximately equal to that of the coil (35 ohms); a low resistance

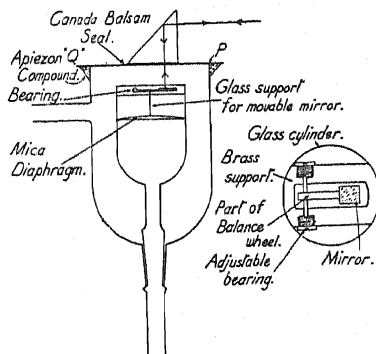


FIG. 2.

rheostat in one of the arms was used for final adjustment of the balance. After balancing the bridge at thermostat temperature, the galvanometer deflection was used to measure rise in temperature. The galvanometer was critically damped, and a resistance of 2000 ohms in series with the battery prevented any appreciable heating of the resistance thermometer by the bridge current. The resistance thermometer was calibrated *in situ* in the wool sample with an atmosphere of water vapour at 23.5 mm.



pressure. This was done by enclosing the sample in a closed copper cylinder in the chamber A, leaving as nearly as possible the same amount

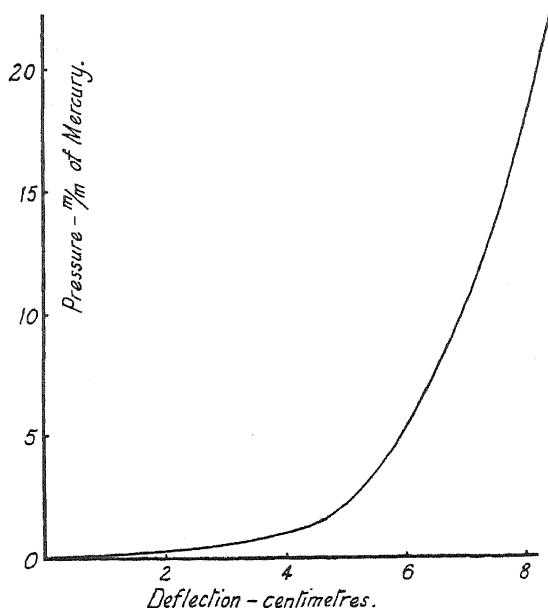


FIG. 3.

Stewardson.<sup>4</sup> The tilting system was made more robust by replacing the knife edge with the bearing of a small clock balance wheel. The gauge itself is fitted into its enclosure by a ground joint and may easily be removed for adjustment or calibration by removing the glass plate P. The sensitivity curve is shown in Fig. 3.

The whole system, including the resistance thermometer bridge, was housed in a large air thermostat which was maintained at  $25^{\circ}\text{C.} \pm 0.2^{\circ}\text{C.}$  by means of a vapour pressure control and mat electric heaters spaced regularly round the walls. Two fans in the roof gave a vigorous air circulation.

Experimental procedure was as follows. The resistance thermometer leads were disconnected and the system pumped out until the wool showed a constant weight. The tap T (Fig. 1), which could be operated

in an experimental run. The cylinder was heated by a coil wound on the outside, and the temperature inside was measured by a calibrated thermocouple. Calibration of the resistance thermometer consisted of heating the cylinder to a constant temperature measured by the thermocouple, and noting the bridge galvanometer deflection.

An aneroid gauge used to facilitate measurement of the lower water vapour pressures is shown in detail in Fig. 2. It was adapted from that described by

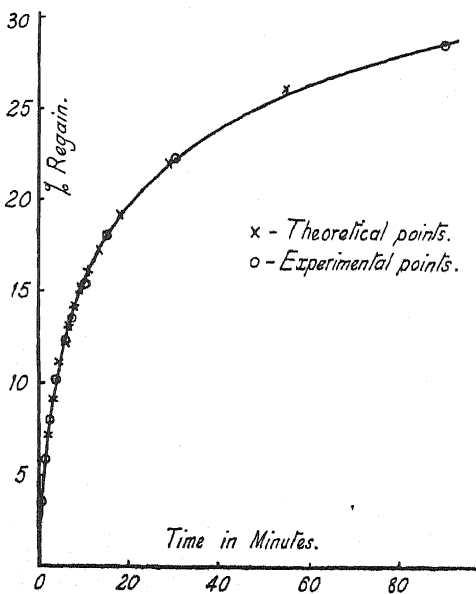


FIG. 4.

<sup>4</sup> Stewardson, *J. Sci. Inst.*, 1930, 7, 7.

from outside the thermostat, was opened and the increase in length of the spring was read off at subsequent time intervals up to 90 minutes. The

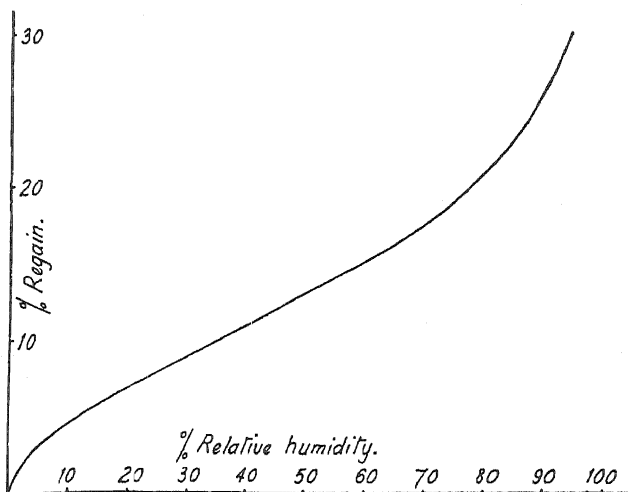


FIG. 5.

regain\* of the wool can be determined from the spring elongation, so that these readings give variation of regain with time as reproduced in Fig. 4.

The equilibrium regain of the wool at water vapour pressures up to 23.5 mm. at 25° C. is also required. This is obtained by introducing increasing amounts of water vapour into the absorption chamber, and measuring the spring elongation and water vapour pressure after a time interval long enough for the wool to return to 25° C.: a constant water vapour pressure indicates that this has been attained. The graph of regain plotted against water vapour pressure for the wool used in these experiments, at a temperature of 25° C., is shown in Fig. 5.

When the determinations of regain were completed, the leads from the resistance thermometer were connected to the bridge circuit, and readings obtained of the temperature of the wool at successive time intervals after opening the tap T. The graph of temperature plotted against the time after opening T is shown in Fig. 6.

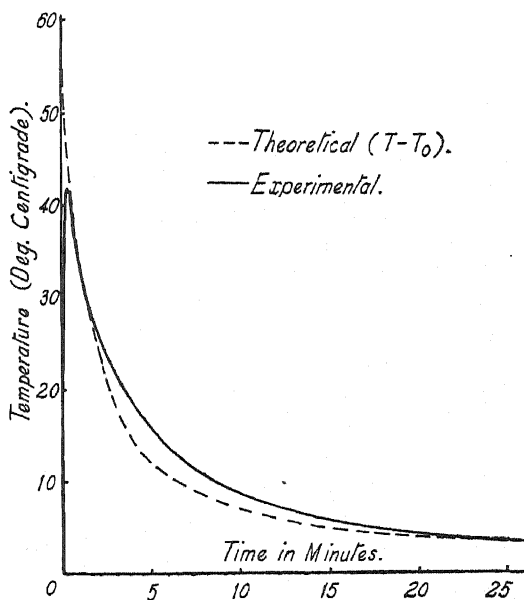


FIG. 6.

\* The percentage water content relative to the dry weight of wool.

Finally, the resistance thermometer was suspended in position, free from wool, and water vapour introduced as before; this gave a measure of heating due to compression of water vapour in the chamber A. The rise of temperature in this case was 3° C., and may be neglected in the present experiment.

### Discussion of Experimental Results.

A glance at Fig. 4 might suggest that despite absence of diffusion wool fibres absorb water vapour slowly; this slowness is not, however, due to a slow diffusion of water into the fibres themselves, but is due to the high temperature attained by the fibres because of the large heat of absorption of water vapour; Fig. 6 shows the temperature increase observed experimentally.

The effect of this increase in temperature on regain of the fibres can be determined from Kirchoff's relation. Shorter<sup>5</sup> and Hedges<sup>6</sup> have shown that this relation applies to absorption of water vapour by wool. It states that if regain is to remain unchanged, the temperature and pressure must be varied according to the relation:

$$\log \frac{p}{p_0} = \frac{Q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right), \quad . \quad . \quad . \quad (1)$$

where  $Q$  is the heat of absorption per mol,  $R$  is the gas constant per mol, and  $T$  and  $T_0$  are the absolute temperatures corresponding to  $p$  and  $p_0$ .

Suppose a mass of wool is contained in an evacuated chamber and water vapour at a pressure  $p$  is suddenly introduced. If a fractional regain  $M$  is instantly acquired by the wool, the rise in temperature of the wool is given by:—

$$\Delta T = q/c \frac{M}{100}, \quad . \quad . \quad . \quad (2)$$

where  $q$  is the heat of absorption per gm. of water vapour and  $c$  is the specific heat per gm. of wool.

Now,  $q$  is large, being roughly 750 cal./g. for dry wool (*cf.* Hedges, 1926), and  $c$  is 0.3 cal./g./°C. An increase in regain from 0 to 2 %, therefore, gives an increase in temperature of 50° C.; and according to equation (1) a large water vapour pressure will be required to give the

TABLE I.—REGAIN AND TEMPERATURE OF WOOL  
SUDDENLY EXPOSED TO AN INCREASE IN WATER  
VAPOUR PRESSURE FROM 0 TO 23.5 MM AT 25° C.  
 $T_0 = 25^\circ \text{C.}$   $p = 23.5 \text{ MM.}$

$p_0 \text{ mm.}$	$M\%$	$T^\circ \text{C.}$	$\left( \frac{q}{c} \times \frac{M}{100} \right) ^\circ \text{C.}$	$(T_0 + \Delta T) ^\circ \text{C.}$
0.235	1.2	104	30	55
0.470	2.0	89	50	75
0.705	2.4	81	60	85

was suddenly introduced. If the temperature of the wool remained at 25° C. its regain would be more than 30 %. But rise of temperature, because of heat of absorption, makes the regain immediately acquired much less. This

sudden increase of regain to 2 % even when the fibres reach equilibrium with the water vapour instantaneously. Take the conditions of the experiment just described. Here, the wool was originally at 25° C. and water vapour at 23.5 mm.

<sup>5</sup> Shorter, *J. Text. Inst. T.*, 1924, **15**, 320.

<sup>6</sup> Hedges, *Trans. Faraday Soc.*, 1926, **22**, 176.

initial regain can actually be determined by assuming the wool to come instantaneously to equilibrium with any water vapour and temperature conditions. Table I shows the calculation.

Column (1) contains water vapour pressures arbitrarily chosen to cover likely values. The second column gives the regains corresponding to these pressures at 25° C.: they are obtained from the experimental curve shown in Fig. 5.  $T$  is obtained from Kirchoff's relation with  $p$  equal to 23.5 mm.; it is the temperature giving equilibrium with the regain of column (2) for  $p$  equal to 23.5 mm. The fourth column is obtained from equation (2). The regain first acquired by the wool when water vapour is introduced will be approximately that where  $T$  equals  $(T_0 + \Delta T)$ ; interpolation in Table I gives a value of roughly 2.3 %. Hence, even though the conditions of the experiment were such that a regain of more than 30 % would be ultimately acquired by the wool, it cannot because of heat of absorption increase instantaneously by more than 2.3 %.

The instantaneous increase of regain on opening the tap  $T$  cannot be accurately determined from the graph of Fig. 4. The first observed point is 15 sec. after introducing the water vapour, and at this time the regain is nearly 4 %. The time required for the fibres to come to equilibrium with the water vapour-temperature conditions in their immediate neighbourhood must, therefore, be considerably less than 15 sec.; how much less, it is impossible to estimate.

Table I shows that the temperature of the wool should rise to roughly 80° C. Experimental observations recorded on Fig. 6 do not give a point much higher than 65° C., but as this temperature was observed 30 sec. after introduction of the water vapour, considerable cooling has clearly taken place: a temperature of 80° C. is not inconsistent with the cooling curve.

As the wool cools down its regain will increase, and a curve for regain versus time can be obtained, assuming the wool always in equilibrium with the water vapour-temperature conditions, and assuming Newton's law of cooling. In these circumstances the heat balance equation is:—

$$c \frac{dT}{dt} = q \frac{dM}{dt} - \nu(T - T_0), \quad . \quad . \quad . \quad (3)$$

where  $\nu$  is a constant.

Integration of (3) gives:—

$$c[\log(T_i - T_0) - \log(T - T_0)] + q \int_{T_i}^T \frac{dM}{T - T_0} = \nu t, \quad . \quad (4)$$

where  $T_i$  is some initial temperature of the wool.

As Newton's law of cooling has been assumed, equation (4) cannot apply for very large temperature differences: it is thus of little use in the region of cooling from 80° C. to 65° C.

The integral is evaluated by finding  $(T - T_0)$  in terms of  $M$  from Kirchoff's relation and the graph of Fig. 5; suitable values of  $M$  are chosen, and  $p_0$  is read from Fig. 5;  $T$  is then obtained from Kirchoff's relation. A graph of  $1/(T - T_0)$  plotted against  $M$  enables the integral to be evaluated. To obtain  $\nu$  the calculated value was fitted with the observed value at the regain of 20 %, or 21 min. after entry of the water vapour.

The calculated values are shown in Fig. 4 for variation of regain with time. The calculated points lie very close to the observed curve,

indicating that the theory is adequate for explanation of the shape of the curve. The calculated point at 26 % regain was obtained from an analytical asymptotic expression for equation (4). At regains in excess of 22 %,  $1/(T - T_0)$  becomes so large that graphical integration is difficult and inaccurate. But if the relation  $dM = \alpha \cdot dp_0$  where  $\alpha$  is a constant be assumed for  $T$  constant, the integral of equation (4) becomes for small values of  $(T - T_0)$  :—

$$\int \frac{dM}{(T - T_0)} = \alpha \frac{Q}{RT_0^2} p \log(T - T_0). \quad (5)$$

Calculations similar to those of columns (1) to (3) of Table II give  $(T - T_0)$  for any chosen values of  $M$ , and equation (5) can then be used to find  $vt$  and  $t$ ;  $\alpha$  is obtained from the regain-relative humidity curve of Fig. 5.

The actual value of the emissivity which gives a fit for calculated and observed values of  $M$  at 21 min. lies between 2 and  $3 \times 10^{-4}$  cal./sq. cm./sec./° C.; the area of the wool sample is difficult to estimate, so that the emissivity cannot be accurately determined, but these limits are in reasonable agreement with values quoted by Preston.<sup>7</sup>

Calculated values of  $(T - T_0)$  are shown with the experimental curve in Fig. 6. The calculated values lie below the observed curve. The agreement is, however, as close as might be expected: the discrepancy is probably due to neglect of any temperature gradient from the centre to the surface of the wool sample. It should be noted that the time scale is much larger in Fig. 6 than in Fig. 4.

One point worth noting is the very small contribution of the specific heat of the wool to the cooling curve compared with that of the heat of absorption; for example, after 20 min. the specific heat contribution to heat loss was only 1/16th that of the heat of absorption contribution. If there was appreciable delay in absorption of water vapour by the fibres, the large heat of absorption contribution would have made the agreement between calculated and observed values very poor.

### Conclusions.

There seems little doubt from comparison of experimental observations and the calculations made on the assumption that the fibres are always in equilibrium with the atmosphere in their immediate neighbourhood, that the shapes of regain-time curves are entirely due to the external factors of diffusion and dissipation of heat, and bear no relation to the diffusion of water into the fibres: in the experiment just described they are merely cooling curves. Quantitatively the experiment has given little data on the rate of pick up of water vapour by wool fibres except that the time to approach equilibrium must be less than 15 sec. None the less the results are very important because they show that in water vapour-temperature exchange between an atmosphere and hygroscopic textile fibres, the time required for the fibres to come to equilibrium with any change in conditions can be wholly neglected compared with the time required for dissipation of heat or diffusion of water vapour. They show, too, that contrary to deductions in various publications, nothing can be learnt of the surface structure of the fibre colloids from study of regain-time curves.

<sup>7</sup> *Preston's Heat*, Macmillan & Co., 3rd edition, p. 506.

### Summary.

A study has been made of the rate of pick up of water vapour by wool fibres when water vapour alone is in contact with the fibres. The time required for the fibres to come to equilibrium with the water vapour when a change of pressure occurs is shown to be entirely dependent on the rate of loss of heat of absorption. When allowance is made for the effect of heat of absorption it is found that the fibres attain equilibrium in a time considerably less than 15 sec. ; how much less cannot be estimated.

The forms of regain-time curves which have hitherto been observed are shown to be determined entirely by the external factors of diffusion and rate of heat loss, and they bear no relation to the structure of the fibre colloids.

The Authors' thanks are due to Mr. J. G. Miller for assistance with the experimental work.

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## PART II.—THEORY OF PROPAGATION OF TEMPERATURE CHANGE.

By A. B. D. CASSIE.

Part I of the present publication has shown that the time required for textile fibres to come to equilibrium with changed water vapour conditions is negligible compared with the time required to remove heat from the fibres to the surroundings. If the textile is immersed in an air-water vapour atmosphere, the time required for the fibres to come to equilibrium with the atmosphere immediately at the fibres will be negligible compared with the time required for transport of appreciable quantities of heat or water vapour through the atmosphere. This has been proved true for heat transport : it will also be true for water vapour transport, as the thermal diffusivity of air is very nearly equal to the diffusion constant of water vapour in air at N.T.P. These hypotheses enable much to be learnt of the propagation of temperature changes through textiles in slowly moving air-water vapour mixtures.

A recent paper by Henry<sup>1</sup> discussing diffusion in absorbing media, includes the mathematics required for the case where a temperature change diffuses through textiles. The present paper covers the case of air flowing through textiles under a mechanically applied pressure difference, and discusses the physical significance of the mathematical results.

### Propagation of Temperature Change when Air flows at a Uniform Velocity through a Semi-infinite Slab of Textile Fibres.

The simplest case to consider is an air-water vapour mixture flowing through a semi-infinite slab of textile fibres. The fibres are supposed conditioned at some definite temperature and water vapour concentration, and at time zero the temperature and water vapour concentration are changed in the incident air.

<sup>1</sup> Henry, *Proc. Roy. Soc., A*, 1939, 171, 215.

Take an element of length  $dx$  in the direction of flow, and of unit cross-section normal to this direction. The equation of heat balance is :—

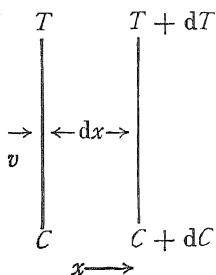


FIG. 1.

$$S \frac{\partial T}{\partial t} = -\rho_a c_a v \frac{\partial T}{\partial x} + q\rho \frac{\partial M}{\partial t},$$

and that of water vapour balance is :—

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} - \rho \frac{\partial M}{\partial t},$$

where  $S$  is the heat required to raise the temperature of 1 c.c. of the air-textile mixture through  $1^\circ \text{C.}$ , assuming no water vapour exchange,  $\rho_a$  the density of air,  $c_a$  the specific heat of air at constant pressure,  $q$  the heat of absorption of 1 gm. of water by the textile,  $\rho$  the mass per c.c. of textile fibres,  $M$  the fractional regain of the fibres,  $C$  the water vapour concentration.  $M$  is assumed to vary linearly with  $T$  and  $C$  (cf. Henry<sup>1</sup>), so that :—

$$\frac{\partial M}{\partial t} = \sigma \frac{\partial C}{\partial t} - \omega \frac{\partial T}{\partial t}, \quad . \quad . \quad . \quad (1)$$

where  $\sigma$  and  $\omega$  are constants. The compressibility of the air is neglected.

Substituting this in the two equations and rearranging, gives :—

$$v \frac{\partial T}{\partial x} + \frac{S}{\rho_a c_a} \frac{\partial T}{\partial t} - \frac{q\rho}{\rho_a c_a} \left[ \sigma \frac{\partial C}{\partial t} - \omega \frac{\partial T}{\partial t} \right] = 0,$$

and

$$v \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \rho \left[ \sigma \frac{\partial C}{\partial t} - \omega \frac{\partial T}{\partial t} \right] = 0,$$

or

$$V \frac{\partial T}{\partial x} + \frac{\partial T}{\partial t} - \alpha \frac{\partial C}{\partial t} = 0 \quad . \quad . \quad . \quad (2)$$

and

$$W \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} - \beta \frac{\partial T}{\partial t} = 0, \quad . \quad . \quad . \quad (3)$$

where

$$V = \frac{v}{(S + q\rho\omega)/\rho_a c_a}; \quad \alpha = q\rho\sigma/(S + q\rho\omega).$$

$$W = \frac{v}{(1 + \rho\sigma)}; \quad \beta = \rho\omega/(1 + \rho\sigma).$$

Equations (2) and (3) can be solved by the method of normal functions. Multiply (2) by  $r/V$  and (3) by  $s/W$  and add; the result is :—

$$\frac{\partial}{\partial x} (rT + sC) + \frac{\partial}{\partial t} \left\{ \frac{r}{V} - \beta \frac{s}{W} T + \left( \frac{s}{W} - \alpha \frac{r}{V} \right) C \right\} = 0. \quad . \quad (4)$$

This can be written as :—

$$u \frac{\partial f}{\partial x} + \frac{\partial f}{\partial t} = 0, \quad . \quad . \quad . \quad (5)$$

where

$$f = (rT + sC), \quad . \quad . \quad . \quad (6)$$

and  $u$  is given by

$$\left( \frac{1}{u} - \frac{1}{V} \right) \left( \frac{1}{u} - \frac{1}{W} \right) = \frac{\alpha\beta}{VW}. \quad . \quad . \quad . \quad (7)$$

Equation (7) shows that there are two values of  $u$ ,  $u_1$ , and  $u_2$ , say, and there are two functions of the form  $f(x, t)$  given by (5). The function  $f(x, t)$  according to equation (5) must be of the form :

$$f(x, t) = g(x - ut). \quad (8)$$

This means that there are two linear combinations of  $C$  and  $T$  which are propagated unchanged in form through the textile with velocities  $u_1$  and  $u_2$ .

Let the functions be  $f_1$  and  $f_2$ , given by :—

$$f_1 = (r_1 T + s_1 C), \text{ and } f_2 = (r_2 T + s_2 C).$$

The ordinary routine for setting up normal functions then gives :—

$$\frac{1}{r_1} f_1 = T + \frac{W}{\beta} \left( \frac{1}{V} - \frac{1}{u_1} \right) C, \quad (9)$$

$$\frac{1}{s_2} f_2 = \frac{V}{\alpha} \left( \frac{1}{W} - \frac{1}{u_2} \right) T + C, \quad (10)$$

or, solving for  $T$  and  $C$ .

$$T = \frac{\frac{1}{r_1} f_1 - \frac{W}{\beta} \left( \frac{1}{V} - \frac{1}{u_1} \right) \frac{1}{s_2} f_2}{1 - \frac{VW}{\alpha\beta} \left( \frac{1}{V} - \frac{1}{u_1} \right) \left( \frac{1}{W} - \frac{1}{u_2} \right)}, \quad (11)$$

$$C = \frac{\frac{V}{\alpha} \left( \frac{1}{W} - \frac{1}{u_2} \right) \frac{1}{r_1} f_1 - \frac{1}{s_2} f_2}{\frac{VW}{\alpha\beta} \left( \frac{1}{V} - \frac{1}{u_1} \right) \left( \frac{1}{W} - \frac{1}{u_2} \right) - 1}. \quad (12)$$

Take the case of a textile conditioned to a fixed temperature and water vapour concentration, and suppose the air flowing through the textile to be suddenly increased in temperature by an amount  $\Delta_0 T$  and the water vapour concentration by  $\Delta_0 C$ . The increases  $\Delta T$  and  $\Delta C$  for subsequent values of  $(x, t)$  are, from equations (11) and (12) :—

$$\Delta T = \Delta_0 T \frac{\left( \frac{1}{V} - \frac{1}{u_2} \right) f_1 - \left( \frac{1}{V} - \frac{1}{u_1} \right) f_2}{\left( \frac{1}{u_1} - \frac{1}{u_2} \right)} + \Delta_0 C \frac{\alpha/V}{\left( \frac{1}{u_1} - \frac{1}{u_2} \right)} (f_2 - f_1), \quad (13)$$

$$\text{and } \Delta C = \Delta_0 T \frac{\beta/W}{\left( \frac{1}{u_1} - \frac{1}{u_2} \right)} (f_2 - f_1) + \Delta_0 C \frac{\left( \frac{1}{V} - \frac{1}{u_2} \right) f_2 - \left( \frac{1}{V} - \frac{1}{u_1} \right) f_1}{\left( \frac{1}{u_1} - \frac{1}{u_2} \right)}, \quad (14)$$



### Physical Interpretation of the Mathematical Results.

Equation (13) with  $\Delta_0 C$  equal to zero answers the problem mathematically and can be used for numerical evaluation of propagation of temperature change. Its physical interpretation throws much light on the processes involved, and makes calculations simpler for many practical problems.

Take the case where  $S = \rho_a c_a$ , so that the textile is regarded merely as a water absorbing medium without otherwise influencing heat exchanges. This assumption introduces little error except in the case of  $u_2$  when numerical values are used, and it makes physical interpretation of the equations much less complicated. The first point is to consider the values of  $V$  and  $W$  compared with  $v$ , the velocity of flow of air through the textile.  $\sigma$  can be obtained from many known graphs of  $M$  plotted against  $C$  for a constant temperature. Its order of magnitude for most textiles and atmospheres common in Britain is  $10^4$  c.c./g.  $\omega$  can be obtained from  $\sigma$  and Kirchoff's relation: for when  $dM$  is zero, equation (1) gives:—

$$\omega = \sigma \frac{dC}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and Kirchoff's condition for constant regain is:—

$$\frac{1}{C} \frac{dC}{dT} = \frac{Q}{RT^2} - \frac{1}{T}, \quad . \quad . \quad . \quad . \quad (16)$$

where  $Q$  is the heat of absorption per mol. of water vapour, and  $R$  is the gas constant per mol.

Equations (15) and (16) give  $\omega$  equal to  $5 \times 10^{-3}/^\circ\text{C.}$  when  $\sigma$  is  $10^4$  c.c./g. Further simplification of the physical discussion is obtained by assuming  $\omega/\sigma$  equal to  $\rho_a c_a/q$ . This happens to be nearly true for normal water vapour concentrations. In this case:—

$$V = W = \frac{v}{(1 + \rho\sigma)}, \quad . \quad . \quad . \quad . \quad (17)$$

and

$$\frac{\alpha\beta}{VW} = \frac{\rho^2\sigma^2}{v^2}. \quad . \quad . \quad . \quad . \quad (18)$$

Substituting these values in the secular equation (7) and noting that  $\rho\sigma$  is of the order of  $2 \times 10^3$ , gives:—

$$\frac{1}{u_1} = \frac{2}{V} = \frac{2}{W} = \frac{2\rho\sigma}{v}, \quad . \quad . \quad . \quad . \quad (19)$$

and

$$\frac{1}{u_2} = \frac{1}{v} \ll \frac{1}{u_1}. \quad . \quad . \quad . \quad . \quad (20)$$

Substitution of  $1/u_1$ , and  $1/u_2$ , from (19) and (20) in equation (13) for the case  $\Delta_0 C = 0$  gives:—

$$\Delta T = \frac{1}{2} \Delta_0 T (f_1 + f_2) \quad . \quad . \quad . \quad . \quad (21)$$

Equation (21) shows that the temperature change is propagated through the textile in two stages: one half the total temperature change passes through the textile at the same speed as the air, and the remaining half is propagated at roughly  $2.5 \times 10^{-4}$  times this speed.

The processes involved when air of constant water vapour concentration flows through a textile with changed initial temperature are now easily described. If the textile had zero specific heat and no hygroscopic property, the temperature change would be propagated at the speed of the air. The hygroscopic properties of the fibres are such, however, that the water vapour concentration as well as the temperature of the air must remain in equilibrium with the textile. If the temperature of the incident air is increased, the fibres also increase in temperature, and the water vapour concentration in the air must be increased by evaporation of water from the textile to maintain equilibrium. If there was no heat of desorption, this would leave the propagation unchanged. But as heat of desorption is required by the fibres, heat must be given by the air to the fibres to maintain the temperature equilibrium. Hence, the air in traversing the textile becomes cooled even though the fibres have zero specific heat. The cooling continues until the water vapour concentration is just that required for equilibrium with the textile at the temperature it assumes, and at its original regain.

Equation (21) shows that this temperature is midway between the initial and final temperatures, and the water vapour concentration in the atmosphere simultaneously increases by  $\omega/\sigma$  times the temperature increase. The new conditions advance just as rapidly as the atmosphere flows through the fibres, because the atmosphere and fibres can produce the change spontaneously when  $\omega/\sigma = \rho_a c_a/q$ .

It is worth noting that the temperature acquired by the air and textile at this stage is determined largely by the properties of the air. Heat of absorption of water vapour by the fibres is the only factor associated with the textile, and this is roughly equal to the latent heat of evaporation of water. The textile can thus be regarded merely as a system for maintaining constant relative humidity in the atmosphere when temperature changes occur. The amount of heat required to evaporate sufficient water into 1 litre of air to maintain a constant relative humidity when the temperature is increased by  $1^\circ\text{C}$ . is roughly equal to the heat obtained by cooling 1 litre of dry air through  $1^\circ\text{C}$ . It is the equality of these two factors operating in opposition that gives a temperature equal to the mean of the initial and final temperatures; if dry air had a greater heat capacity, the temperature attained would be nearer the final than the initial temperature.

The rate of propagation of this intermediate temperature equals the rate of flow of the air if the specific heat of the textile is zero and  $\omega/\sigma$  equals  $\rho_a c_a/q$ . The incident air supplies the heat required for the evaporation of water vapour by dropping its temperature to the mean of the original and final values; the air passing through the textile is adjusted by this temperature drop and corresponding increase in water vapour concentration to be in equilibrium with the textile, which it meets conditioned to the original temperature and water vapour concentration; further heat or water vapour exchange is unnecessary, and the front between the original and intermediate temperatures moves along with speed  $v$ . The finite specific heat of the textile will, in practice, give a slower rate of propagation.

The regain of the textile has not changed appreciably at this stage, but it is continually losing water to the atmosphere, so that after a much longer period the regain is changed sufficiently to be conditioned to equilibrium with the incident air temperature and water vapour concentration. The assumptions made in deducing the mathematical equations

imply that there is a sharp front between the regions of unchanged and changed regain: thus the slow component represents propagation of change of regain, whilst the fast one represents propagation of temperature and water vapour changes without change of regain.

The same processes are followed if concentration is increased whilst temperature remains constant: one front passes rapidly through the textile and across it roughly one half of the total concentration change occurs; the slower front follows bringing the second half of the concentration change and the total regain change. The faster front also brings with it an increase in temperature which disappears as the slower front proceeds; this corresponds with the first term in equation (14).

### Summary.

Mathematical theory is given for the propagation of temperature and water vapour concentration changes through textile materials when an air-water vapour mixture flows through the textile under a mechanically applied pressure difference. The results show that a change in temperature or concentration is propagated through the textile with a fast and a slow component. The physical significance of the two components is discussed.

## PART III.—EXPERIMENTAL VERIFICATION OF THEORY.

By A. B. D. CASSIE AND S. BAXTER.

Part II has shown that temperature change of an air-water mixture is propagated through textiles in a peculiar and distinctive way when the water vapour concentration of the mixture entering the textile is kept constant. A thermocouple measuring the temperature in the bulk

of the textile should show a rapid increase to a temperature roughly midway between the initial and final values; thereafter the temperature should remain constant for a considerable period, after which it should rise rapidly to the final value.

The graph for the ideal case discussed mathematically in Part II, is shown in Fig. 1. There are various simplifying assumptions in the theory, but the most important one which cannot be allowed for experimentally is that all the air passes through the textile with one velocity,  $v$ . This condition cannot be maintained, for flow

through textiles always gives rise to channelling and a distribution of velocities. Again, the theory assumes that the air flows in parallel straight lines through the textile, whereas the actual path must be zig-zag, giving a distribution of path lengths between any two planes normal to the general direction of movement of the air. The effect of varying velocities and path lengths will be to round off the sharp curve shown in Fig. 1. The distinctive features of the curve should, however, be well

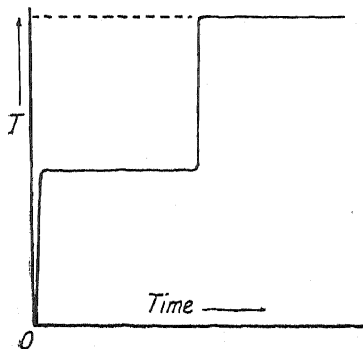


FIG. 1.

maintained in any experimental results, and these should readily show whether or not the theory is correct.

### Experimental.

The only precaution necessary in the experimental design is avoidance of any large heat capacity in contact with the textile fibres. It was shown in Part II that the relative value of the heat capacity of the atmosphere and the heat of sorption is largely responsible for the shape of the temperature-time curve, and introduction of any object of appreciable heat capacity changes this relationship, and must change the shape of the theoretical curve. The test body A, B, C, D, Fig. 2, was, therefore, made entirely of textile materials apart from a thin coating of cellulose varnish over the ends A, D and B, C to prevent air streaming through the ends.

The test body consisted of two concentric starched linen cylinders with the textile fibre packed as uniformly as possible between the two. The inner cylinder was first made and a sliver of the textile wound round it: starched linen was then wound round the outside, and end caps, also of linen, were fitted. Starched linen was used so that the cylinders would keep their shape, and give surfaces independent of the actual textile fibre under investigation. The top end of the inner tube fitted a double-walled glass tube, and the seal between the two was made airtight with cellulose varnish.

The test body was housed in a brass cylinder, K, L, M, N, and this could be immersed in either of two thermostats kept near  $15^{\circ}\text{C}$ . and  $30^{\circ}\text{C}$ ., respectively. Air was passed through long spirals in the thermostats before entering the brass cylinder at E. The vapour pressure of the entering air was kept constant by bubbling one fraction of it through water maintained at the temperature of the cold thermostat, whilst the other fraction passed over  $\text{CaCl}_2$ . Before passing to the spirals in the thermostats the air passed over a hair hygrometer and thermometer, which checked the water vapour pressure, and through a flow-meter which checked the rate of flow.

The procedure in making a run was as follows: the brass cylinder with its textile cylinder was immersed in the cold thermostat and coupled to the spiral in that thermostat. Air from the flow meter was coupled to the other end of the spiral. The air was allowed to flow through the test body and escaped at F until the thermo-couples  $T_1$  and  $T_2$  showed identical temperatures. When these thermo-couples show the same temperature, the fibres must be in equilibrium with the air-water vapour mixture at the lower temperature and at the chosen water vapour pressure. The brass cylinder was then transferred to the warm thermostat and the air flow coupled to the spiral in this thermostat. Readings were made of  $T_1$  and  $T_2$  at convenient intervals after the beginning of the air flow through this thermostat.

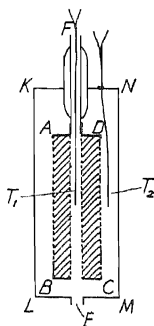


FIG. 2.

### Experimental Results and their Interpretation.

The theory of Part II has been worked out for a semi-infinite slab of textile material, whilst the test pieces formed concentric cylinders. It is easily proved by using cylindrical co-ordinates that the same formulæ hold if the velocity of the gas is put equal to the volume traversing per second unit area of the cylinder whose radius is the mean of the outer and inner cylinders. Thus, if  $a$  and  $b$  are the radii of the inner and outer cylinders, the velocity of the gas is obtained from the volume traversing

unit area of the cylinder of radius  $\frac{1}{2}(a + b)$  per second; the formulæ are then the same as for propagation through a layer of thickness  $(b - a)$ .

(a) Wool.—Fig. 3 shows a temperature-time curve for a cylinder of wool. The speed of the air through the cylinder of radius  $\frac{1}{2}(a + b)$  was 1.4 cm./sec., and  $(b - a)$  was 1 cm. The water vapour pressure was 11 mm., and the temperature of the cold bath was 17.1° C. Curves (A) and (B) show respectively the temperature of the air before and after traversing the wool. The general shape of (B) is as theory predicts.

The relative humidity of the air traversing the wool varies from 75 % at the lower temperature to 32.5 % at the higher temperature, 31° C. The appropriate values of  $\sigma$  and  $\omega$  are  $10 \times 10^3$  c.c./g., and  $6.5 \times 10^{-3}/^\circ\text{C}.$ , respectively. The density of the wool in the cylinder was 0.10 g./c.c. Equation (7) (*cf.* Part II) gives for this case:—

$$u_1 = 5.7 \times 10^{-4} \text{ cm./sec.}; \text{ and } u_2 = 1.4 \times 10^{-2} \text{ cm./sec.}$$

where the specific heat of the wool is taken as 0.35 cal./g./°C., and the heat of absorption of water vapour by wool is 650 cal. per gm. of water absorbed.<sup>1</sup>

Equation (13) of Part II gives:—

$$\Delta T = \Delta_0 T (0.62f_1 + 0.38f_2) \quad (1)$$

The values of  $u$  show that two fronts of temperature change are propagated through the wool: one at speed  $1.4 \times 10^{-2}$  cm./sec., corresponding to  $f_2$ , and another at  $5.7 \times 10^{-4}$  cm./sec., corresponding to  $f_1$ . The value of  $(b - a)$  in the test piece was 1 cm., so that the times required by the fronts to traverse the wool are 70 sec. and 30 min. The total temperature change,  $\Delta_0 T$ , was 13.9° C. and according to equation (1), 5.3° C. should be associated with the faster front, and 8.6° C. with the slower front. The break in the temperature-time curve should thus

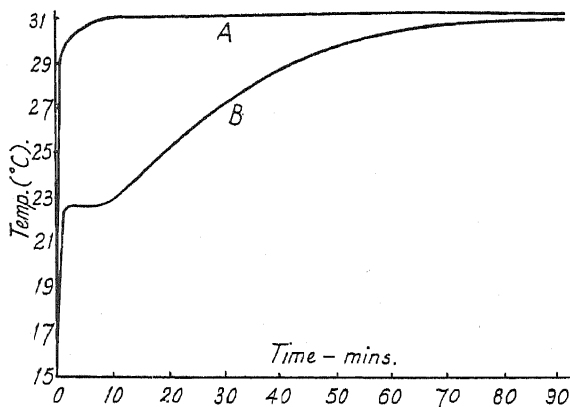


FIG. 3.—Wool, Density 0.10 gms./cc. Water vapour pressure = 11 mm. A.—Air temperature before passing through a cylinder of wool. B.—Air temperature after passing through a cylinder of wool.

appear at 22.4° C. This is verified with surprising accuracy by the experimental curve of Fig. 3.

The time of 70 sec. required for the faster front to pass through the cylinder is rather small for accurate measurement, as roughly 1 min. is required for the entrant air to attain its equilibrium value. 70 sec. actually fits the experimental curve well, but this agreement should not be regarded as more than qualitative. The calculated value is also liable

<sup>1</sup> Hedges, *Trans. Faraday Soc.*, 1926, **22**, 178.

to error as it is given by the difference of two nearly equal quantities, neither of which is accurately known.

The slower front can be followed quantitatively, as is shown by curve (B), Fig. 3. It has the general shape predicted by theory. Lack of sharpness in this curve is most likely due to a distribution of air speeds through the cylinder. This hypothesis can be tested in the following way. If  $f(v)$  be the velocity distribution in the air passing through the cylinder, it will also be the distribution of the speeds of the front; for  $u_1$  is directly proportional to  $v$ . At any time,  $t$ , the fraction of air issuing from the cylinder at the higher temperature is:—

$$F = \int_0^{(b-a)/t} f(u_1) du_1. \quad (2)$$

The temperature of the issuing air will be:—

$$T = (22.4 + 8.6F)^\circ \text{C.}$$

or  $F$  varies linearly with  $T$ . Hence, if  $T$  be plotted against  $(b-a)/t$ , the curve will be the integral of the velocity distribution curve. This is done on curve (A), Fig. 4, for the present case of  $(b-a)$  equal to 1 cm.

The slopes of this curve give (B), Fig. 4. The curve is not symmetrical; that for cotton (Fig. 6B) gives a much better form of distribution curve. The curve for wool may be distorted because regain plotted against temperature for a constant water vapour concentration departs considerably from the linear relation assumed in the theory of Part II. Another factor may be the packing of the wool sliver: cotton, because of its less rigid fibres, packs more easily and more uniformly.

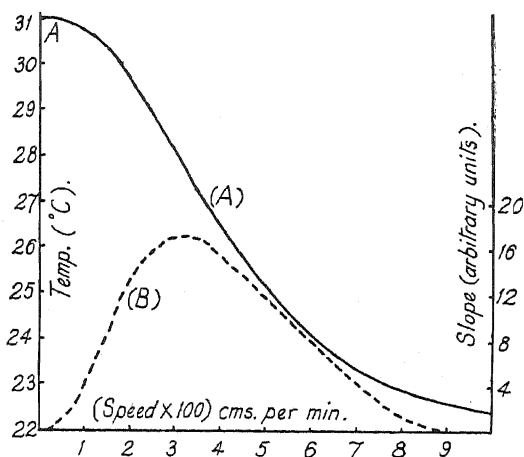


FIG. 4.—Distribution of air speeds through wool cylinder and the integral of distribution curve.

The maximum of curve (B), Fig. 4, lies around the speed  $3 \times 10^{-2}$  cm./min. This gives a time of propagation of 33 min. against the calculated value of 30 min. The agreement is as good as can be expected. A correction should be applied to the calculated value to allow for expansion of the air as it passes through the cylindrical plug. The pressure difference across this was, however, only  $\frac{1}{2}$  mm. of Hg, and the correction is negligible.

(b) **Cotton.**—Similar experiments were made with cotton cylinders, and the temperature-time curve is shown in Fig. 5. Details for this experiment were:—

- Density of cotton,  $\rho$  = 0.12 g./c.c.
- Air speed,  $v$  = 1.4 cm./sec.
- Cold bath temperature = 16.1° C.
- Hot bath temperature = 29.9° C.

Cotton conditioned at 75 % R.H. and 16.1° C.

$$\sigma = 6 \times 10^3 \text{ c.c./g.}$$

$$\omega = 3.9 \times 10^{-3} / ^\circ\text{C.}$$

$$q = 600 \text{ cal./g. water vapour absorbed.}$$

Cylinder wall thickness = 1 cm.

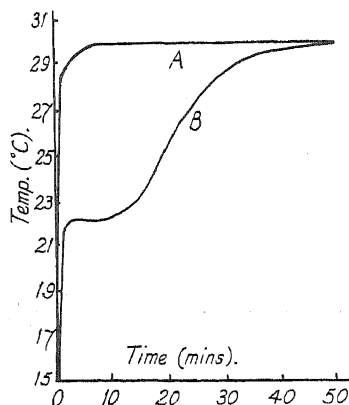


FIG. 5.—Cotton, Density 0.12 gm/u. Water vapour pressure = 10 mm. A.—Air temperature before passing through a cylinder of cotton. B.—Air temperature after passing through a cylinder of cotton.

These values give :—

$$u_1 = 7.75 \times 10^{-4} \text{ cm./sec. ;}$$

$$u_2 = 1.64 \times 10^{-2} \text{ cm./sec.}$$

and the equation for the temperature-time curve is :—

$$T = 16.1^\circ \text{ C.} + (8.7f_1 + 5.1f_2)^\circ \text{ C.}$$

The thickness of the cylinder was again given by  $(b - a)$  equal to 1 cm. The fast component should, therefore, traverse the cylinder in 61 sec. This is of the order shown by experiment, though for reasons previously discussed, the agreement can only be regarded as qualitative. The rapid increase of temperature should cease at 21.2° C. It actually ceases at 22.1° C., so that the agreement here is not so good as for the wool cylinder; it is, nevertheless, good

agreement when the assumptions of the theory are recalled.

A distribution of velocities curve has been obtained for cotton in the same way as it was obtained for wool. It is shown in Fig. 6 (B). It is much more symmetrical than that obtained for wool, and shows a reasonable range of speeds. The maximum occurs near a speed of  $4.5 \times 10^{-2}$  cm./min., corresponding to a time of propagation of roughly 22 min. The time of propagation through 1 cm. given by the calculated value of  $u_1$  is 21 min. The agreement is again surprisingly good.

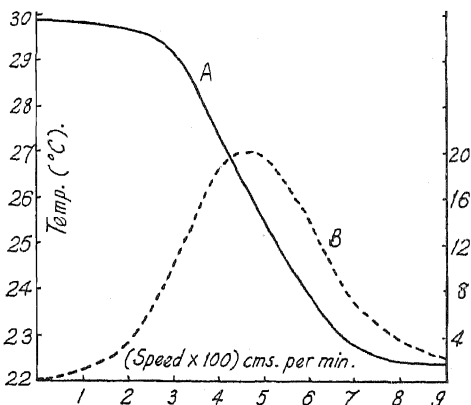


FIG. 6.

### Verification of Henry's Formulæ for Diffusion in Absorbing Media.

Henry<sup>2</sup> obtained formulæ for the diffusion of water vapour concentration and temperature changes into absorbing media. He found that there should be a "temporary wave" which develops quickly, and a main "wave" which develops much more slowly. His "temporary

<sup>2</sup> Henry, *Proc. Roy. Soc., A*, 1939, 171, 215.

wave" increased and finally decreased to zero. Attempts to observe the "temporary wave" were unsuccessful. The conception of a temporary "wave" arises from the form in which Henry used the final diffusion equations. His formula for  $\Delta T$  is:—

$$\Delta T = \Delta_0 T f_2 - \frac{(1 - \mu_2^2 D) \Delta_0 T - \nu \Delta_0 C}{D(\mu_1^2 - \mu_2^2)} (f_2 - f_1), \quad (3)$$

where  $\mu_1$  and  $\mu_2$  are solutions of the secular equation:—

$$\left(\mu^2 - \frac{1}{D}\right) \left(\mu^2 - \frac{1}{D}\right) = \frac{\lambda \nu}{D D'},$$

$D$  is given by

$$D = \frac{D''}{(1 + \rho \sigma)},$$

and  $D''$  is the diffusion coefficient of water vapour through the medium without absorption.

$D$  is given by

$$D = \frac{D''}{(1 + q/c\omega)},$$

where  $D''$  is the thermal diffusivity with no absorption and  $c$  is the specific heat of the absorbing medium

$$\lambda = \frac{\rho \omega}{1 + \rho \sigma} \quad \text{and} \quad \nu = \frac{q/c\sigma}{1 + q/c\omega}.$$

The term  $(f_2 - f_1)$  in equation (3) represents Henry's "temporary wave," but equation (3) can equally be written in the form:—

$$\begin{aligned} & \left[ 1 - \frac{(1 - \mu_1^2 D)(1 - \mu_2^2 D)}{\lambda \nu} \right] \Delta T \\ &= \Delta_0 T \left[ -\frac{(1 - \mu_1^2 D)}{(1 - \mu_2^2 D)} f_1 + f_2 \right] + \Delta_0 C \frac{(1 - \mu_1^2 D)}{\lambda} (f_1 - f_2), \quad (4) \end{aligned}$$

and the equation for water vapour concentration change becomes:—

$$\begin{aligned} & \left[ 1 - \frac{(1 - \mu_1^2 D)(1 - \mu_2^2 D)}{\lambda \nu} \right] \Delta C \\ &= \Delta_0 C \left[ f_1 - \frac{(1 - \mu_1^2 D)}{(1 - \mu_2^2 D)} f_2 \right] + \Delta_0 T \frac{(1 - \mu_2^2 D)}{\nu} (-f_1 + f_2). \quad (5) \end{aligned}$$

Equations (4) and (5) are similar to equations (14) and (15) of Part II. When  $\Delta_0 C$  is zero, a sudden temperature change gives a rapid and a slow component for diffusion of the temperature change into the material, just as was obtained for the air-water mixture flowing through the material.

The magnitudes of the two are again almost equal for textiles; in fact, numerical values inserted in equation (4) give, for  $\Delta_0 C$  zero, for cotton at a density of 0.12 g./c.c. :—

$$\Delta T = \Delta_0 T (0.55 f_1 + 0.45 f_2) \quad (6)$$

Henry called  $f_1$  the "permanent wave," and included  $f_2$  entirely in  $(f_2 - f_1)$  as a "temporary wave." This seems to us misleading as  $f_2$  contributes roughly as much to the permanent temperature change as



does  $f_1$ . Similarly, for a concentration change,  $f_2$  contributes as much as  $f_1$ , although the regain of the material depends almost exclusively on  $f_1$ . Equations (4) and (5) do contain terms in  $(f_1 - f_2)$  which are "temporary," but they are rather different from Henry's terms; a change in temperature produces a temporary change in concentration. The significance of this concentration change has been discussed in Part II. There is an equivalent transient temperature change when concentration is varied; this has also been discussed in Part II.

Henry<sup>2</sup> was concerned with the diffusion of a water vapour change into a bale of cotton, and tried to verify his formulæ for this case. Unfortunately, water vapour changes are exceedingly difficult to measure in the bulk of a textile material. Changes of temperature, on the other hand, are easily measured, and give the simplest means of verifying Henry's formulæ. We have made a rough check of formula (4) with the apparatus used to check the case of the air-water vapour mixture flowing through the textile. The only change necessary to convert the apparatus for diffusion measurements was to seal the top of the central linen cylinder and allow the air-water vapour mixture to flow over the

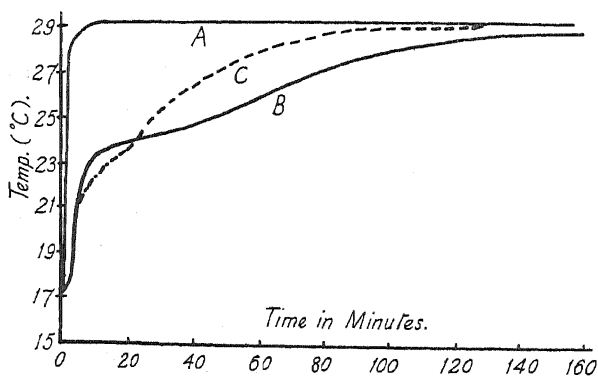


FIG. 7.—Cotton, Density 0.12 gms./cc. Water vapour pressure = 11.2 mm. A.—Outer air temperature. B.—Observed temperature at centre of cylinder. C.—Calculated temperature at centre of cylinder.

sides of the outer linen cylinder. The procedure in making an experiment was then exactly as in the previous case. The results are shown in Fig. 7, curve (B), for cotton fibres at a density of 0.12 g./c.c.

In this case  $f_1$  and  $f_2$  are solutions of the diffusion equation in cylindrical co-ordinates using  $1/\mu_1^2$  and  $1/\mu_2^2$  as diffusion coefficients. Hill<sup>3</sup> has given solutions for this equation, and their use in formula (4) gives curve C of Fig. 7. It should be noted that the time scale is much smaller in Fig. 7 than in Figs. 3 and 5.

Theory and experiment again agree on the presence of fast and slow components. The discussion given for the case of flow through the material is clearly applicable to the present case. One feature of curves (B) and (C) that might seem unexpected is that the theoretical curve is faster than the observed one. This, however, is due to the outer linen cylinder. The density of this material was 0.7 g./c.c. as compared with 0.12 g./c.c. for the bulk of the cotton. The high density would not effect the results very greatly if the air-water vapour mixture had complete access to the cotton, but only one-third of the linen mesh was open, so that constant temperature conditions could not be maintained all over the outside of the cotton. The slow observed rate of diffusion is clearly

<sup>3</sup> Hill, *Proc. Roy. Soc., B*, 1928, 104, 39.

due to this difficulty, for theory assumes that the atmosphere next the cylinder is always fully maintained at the new conditions. Apart from this, the experiment confirms Henry's formula very well, and emphasises again the very great importance of water vapour in the atmosphere for propagation of a temperature change through textiles.

The transient temperature change that occurs when  $\Delta_0 C$  is finite and  $\Delta_0 T$  zero was observed when conditioning the cotton cylinder before beginning an experimental run; in fact, disappearance of the transient temperature change was always used as an indication that the cylinder was properly conditioned.

### Summary.

Experiments are described which verify for wool and cotton the theory of propagation of temperature changes in textiles given in Part II.

The formulæ developed by Henry for the case of diffusion have been verified for cotton. Henry's final formulæ have been rearranged to fit more readily with their physical interpretation and with experimental results.

The authors' thanks are due to the late Dr. B. E. Atkins, who carried out the early experiments, and to Mr. F. Morris, who has assisted in all the experimental work.

The authors of Parts I, II and III wish to express their thanks to Mr. B. H. Wilsdon, Director of Research, for suggesting the investigation, and for discussion throughout the course of the work. Their thanks are also due to the Council of the Wool Industries Research Association for permission to publish this account.

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Torridon, Headingley,  
Leeds, 6.*

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## THE RATE OF REACTION OF SODIUM ATOMS WITH POLYHALOGENATED METHANE DERIVATIVES.

BY J. N. HARESNAPE, J. M. STEVELS AND E. WARHURST.

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Up to the present date relatively few measurements have been made of the velocity of reactions of Na atoms with organic halides which contain more than one halogen atom. The few existing measurements of Hartel, Meer and Polanyi<sup>1</sup> and Heller and Polanyi<sup>2</sup> are exclusively concerned with chlorine derivatives. These authors have measured the rate of reaction of Na atoms with the compounds of the series  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , and found a marked progressive increase in reaction rate on passing along the series from  $\text{CH}_3\text{Cl}$  to  $\text{CCl}_4$ . Heller and Polanyi<sup>2</sup>

<sup>1</sup> Hartel, Meer and Polanyi, *Z. physik. Chem., B*, 1933, **19**, 139.

<sup>2</sup> Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

drew attention to the fact that this increase in reaction velocity runs parallel to a decreasing force constant for the C—Cl bond. It has been shown by one of us (J.M.S.<sup>3, 4</sup>) that in the case of the above series, increase of the number of Cl atoms causes an increase in the atomic refractions and polarisabilities of the individual Cl atoms. Thus, this increase in polarisability runs parallel to the increase in the velocity of the reaction with Na atoms. A general method has been developed<sup>3, 4</sup> for the calculation of the atomic refraction of any halogen atom in any polyhalogenated methane derivative. In the case of the mixed methane derivatives containing C, H, Cl and Br certain well marked trends in polarisability of the halogen atoms are noticeable, and in view of this it is of considerable interest to measure the rates of reaction of these derivatives with sodium atoms in order to correlate trends of reaction rates with these trends in polarisability. The field chosen for investigation consisted of ten of the possible fourteen methane derivatives which contained chlorine or bromine or both halogens together. The compounds  $\text{CCl}_2\text{Br}_2$  and  $\text{CClBr}_3$  were omitted because of their instability and  $\text{CBr}_4$  on account of its low vapour pressure;  $\text{CH}_3\text{Cl}$  was also not included. In addition to these ten compounds, two methane derivatives containing F and Br, *viz.*  $\text{CHFBr}_2$  and  $\text{CFBr}_3$  have been dealt with, together with methyl iodide.

### Experimental.

The halides were prepared in the Physical Chemistry Department of the University of Leiden; the methods of preparation and purification are described elsewhere.<sup>5</sup> Two different experimental methods were employed to measure the reaction rates, (a) the Life Period Method<sup>6, 7</sup> with the modifications described recently by one of the authors,<sup>8</sup> and (b) the Diffusion Flame Method as modified by Heller.<sup>9</sup> In both cases the halides were used in pairs, *i.e.* in the same run the reaction rates of halides A and B were measured, and in the next run the rates of B and C, and so on. From the ratios of the rates so obtained, by choosing one halide as standard, a gradation of relative velocities along a series could be obtained. In this way the effect of errors which might vary haphazardly from run to run was eliminated as far as possible. This was essential since in some cases the difference in reaction rates is not very great. This procedure gives an accurate gradation of velocity constants, the accuracy being independent of any uncertainties in the absolute values of the constants. The purity of all the compounds was checked before use by refractive index measurements.

### The Life Period Method.

The technique employed was that which has been described for measurements of the rate of reaction of Na atoms with bromobenzene.<sup>8</sup> Hydrogen was the carrier gas and its rate of flow was regulated in all experiments so that  $v/\delta \sim 13 \times 10^{-2}$  where  $v$  is the linear streaming velocity of the carrier gas at the nozzle mouth in metres/per sec., and  $\delta$  is the diffusion constant of the Na vapour in the carrier gas at the pressure in the reaction vessel ( $\sim 3$  mm.). The temperature of the Na boat was usually about  $192^\circ \text{C}$ . These conditions are within the range which has been shown by one of us<sup>8</sup> to lead to very reliable results with the Life Period Method. The majority

<sup>3</sup> Stevels, *Trans. Faraday Soc.*, 1937, **33**, 1381.

<sup>4</sup> *Ibid.*, 1938, **34**, 429.

<sup>5</sup> Stevels, *Dissertation*, Leiden, 1937.

<sup>6</sup> Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

<sup>7</sup> Fairbrother and Warhurst, *ibid.*, 1935, **31**, 987.

<sup>8</sup> Warhurst, *ibid.*, 1939, **35**, 674.

<sup>9</sup> Heller, *ibid.*, 1937, **33**, 1556.

of the velocity constants diverged from the mean value by less than  $\pm 10\%$ ; in a few cases greater divergencies were obtained. In some experiments velocity constants were determined over a range of flame sizes corresponding to 14 % to 20 % absorption. No drift in the value of the constant was apparent. In the case of  $\text{CH}_2\text{Br}_2$  the constant was determined with a sodium temperature of  $191^\circ\text{C}$ . and subsequently with a temperature of  $220^\circ\text{C}$ ., corresponding to more than a five-fold increase in sodium vapour pressure. The two sets of values were in good agreement. A typical batch of results is shown in Table I, which illustrates the points mentioned above.

TABLE I.—REACTION VESSEL TEMPERATURE  $255^\circ\text{C}$ .

Compound.	% Absorption of Flame.	Temp. of Sodium $^\circ\text{C}$ .	Velocity Constant $k(\times 10^{-12})$ cc. mol $^{-1}$ , sec. $^{-1}$
$\text{CH}_2\text{Cl}_2$	16.9	192	0.60
	17.0	192	0.59
$\text{CH}_2\text{ClBr}$	15.6	192	17.8
	14.5	192	16.6
	20.8	192	16.4
	19.9	192	18.7
$\text{CH}_2\text{Br}_2$	17.5	192	31.0
	18.0	192	31.4
	13.3	192	25.0
	14.0	192	29.8
$\text{CH}_2\text{Br}_2$	19.0	192	48.5
	21.0	192	41.7
	17.5	191	59.0
	17.2	191	57.5
	17.3	220	46.0
	19.0	220	45.0
$\text{CFBr}_3$	18.8	220	43.0
	15.1	224	91.0
	13.9	224	89.7

### The Diffusion Flame Method.

The first experiments were carried out using nitrogen as carrier gas at pressures ranging from 3.15 mm., and sodium temperatures of about  $240^\circ\text{C}$ . The results obtained under these conditions were unsatisfactory, the velocity constants showing a pronounced decrease with increase of nitrogen pressure in the reaction vessel (see Table II).

TABLE II.— $\text{CHClBr}_2$ . REACTION VESSEL TEMPERATURE  $250^\circ\text{C}$ .

Nitrogen pressure, $P_{\text{N}_2}$ in mm.	2.6	4.0	4.0	3.9	5.0	5.1	7.2	7.5	11.3
Vel. const. $k \times 10^{-12} \frac{\text{cc}}{\text{mol. sec.}}$	42	22	19	20	16	14	10.6	10.3	6.9

This drift of  $k$  with  $P_{\text{N}_2}$  was most marked for the halides which reacted fastest. The explanation of this drift lies in the fact that the flames prove to be far from ideal since they largely consisted of a central core of unreacting sodium atoms into which no halide was able to diffuse ("core" flames), because the ratio of the partial pressure of halide,  $P_{\text{Hal}}$ , to the sodium pressure,  $P_{\text{Na}}$ , at the nozzle mouth was very small ( $\sim 1/3$ ). In order to change this state of affairs a modification in experimental technique was made. The velocity constant of the reaction is given by

$$k = \frac{\left( \ln \frac{P_{\text{Na}}}{P_{\text{Na}}^0} - \ln \frac{R}{r} \right)^2}{(R - r)^2} \frac{\delta}{P_{\text{Hal}}}$$

where  $P_{\text{Na}}$  is the sodium pressure at the nozzle mouth,  $P_{\text{Na}}^0$  the limiting pressure of sodium visible,  $R$  the radius of the flame,  $r$  the radius of the

nozzle,  $\delta$  the diffusion constant of sodium vapour, and  $P_{\text{Hal}}$  the partial pressure of halide in the reaction vessel. Thus, other things being equal an increase in  $P_{\text{Hal}}$  necessitates a proportional increase in  $\delta$  for the same stationary state (*i.e.* flame diameter) to be maintained. A considerable increase in the ratio of  $P_{\text{Hal}}/P_{\text{Na}}$  was brought about by a twenty fold increase in  $\delta$ . This was achieved by using hydrogen instead of nitrogen as carrier gas at very low pressures (as low as 0.4 mm.) in the reaction vessel. The correct value of  $v/\delta$  was maintained by using very high speeds of flow of carrier gas; such speeds were made possible by placing a reaction vessel on the low pressure side of three mercury vapour circulation pumps working in parallel. The tendency to form "core" flames was further reduced by lowering the sodium pressure at the nozzle mouth from  $2 \times 10^{-3}$  to  $4 \times 10^{-4}$  mm.

The results with the new conditions for  $\text{CHCl}_2\text{Br}$ , a very reactive compound, are shown in Table III, for various carrier gas pressures,  $P_{\text{H}_2}$ , in the reaction vessel. Although the results vary considerably, on account

TABLE III.—TEMPERATURE OF REACTION VESSEL 250° C.

$P_{\text{H}_2}$ in mm.	0.43	0.46	0.46	0.47	0.54	0.55	0.55	0.71	0.94
$k \times 10^{-12}$	115	132	130	174	124	104	97.3	130	88.4

of increased difficulty in measuring accurately flames of such low intensity, there is no apparent drift in the value of  $k$  over a more than two-fold increase in  $P_{\text{H}_2}$ . The value of the ratio of  $P_{\text{Hal}}/P_{\text{Na}}$  in this case was  $\sim 4$ . The new value of  $k$  for  $\text{CHClBr}_2$  (the early results for which are shown in Table II) proved to be  $180 \times 10^{12}$ . On account of the decreased dazzling effect on the eye of the central zone of the resonance flames in these experiments at low Na pressures we consider that the appropriate value for  $P_{\text{Na}}^0$  is  $7 \times 10^{-6}$  mm.

The results obtained by the Life Period and Diffusion Flame Methods

TABLE IV.

Compound.	Collision Yield Life Period Method.	Collision Yield Diffusion Flame Method.
$\text{CCl}_4$	5.3	5.5
$\text{CCl}_2\text{Br}$	5.3	1.7
$\text{CHCl}_3$	—	50
$\text{CHCl}_2\text{Br}$	13.5	4.4
$\text{CHClBr}_2$	9.0	2.8
$\text{CHBr}_3$	6.3	1.4
$\text{CH}_2\text{Cl}_2$	833	760
$\text{CH}_2\text{ClBr}$	28	26
$\text{CH}_2\text{Br}_2$	17.0	13.2
$\text{CH}_3\text{Br}$	—	135
$\text{CHFBr}_2$	11	—
$\text{CFBr}_3$	5.5	2.3
$\text{CH}_3\text{I}$	10.6	11.4

are given in Table IV and are shown schematically in Table V. In Table V the figure underlined above each compound is the collision yield, *i.e.* the average number of collisions per effective collision; the values are those of the Diffusion Flame Method. In calculating these collision yields the value of the collision cross-section of  $3.5 \times 10^{-15}$  cm.<sup>2</sup> given by Hartel and Polanyi<sup>10</sup> was used. This value is probably somewhat high for monohalogenated compounds.<sup>8</sup> The collision yield for methyl chloride (marked\*) has been taken from the work of Heller and Polanyi.<sup>2</sup> The figure

below each compound is the atomic refraction calculated by the method developed by one of the authors.<sup>3, 4</sup> In the cases of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  the refractions given are per chlorine atom; in all other cases

<sup>10</sup> Hartel and Polanyi, *Z. physik. Chem., B*, 1930, 11, 97.

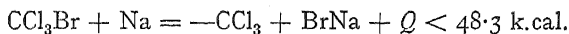
the refractions are per bromine atom since, in these cases, the reaction consists in the removal of a bromine atom. The values for the two series  $\text{CH}_3\text{Cl} \rightarrow \text{CCl}_4$  and  $\text{CH}_3\text{Br} \rightarrow \text{CBr}_4$  have been published previously by one of us.<sup>3</sup>

TABLE V.

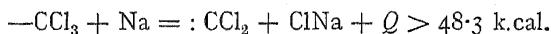
$\begin{array}{c} 5.5 \\ \text{CCl}_4 \\ 6.61 \end{array}$	$\begin{array}{c} 1.7 \\ \text{CCl}_3\text{Br} \\ 8.88 \end{array}$	$\begin{array}{c} 9.17 \\ \text{CCl}_2\text{Br}_2 \end{array}$	$\begin{array}{c} 9.46 \\ \text{CClBr}_3 \end{array}$	$\begin{array}{c} 9.75 \\ \text{CBr}_4 \end{array}$
$\begin{array}{c} 50 \\ \text{CHCl}_3 \\ 6.47 \end{array}$	$\begin{array}{c} 4.4 \\ \text{CHCl}_2\text{Br} \\ 8.65 \end{array}$	$\begin{array}{c} 2.8 \\ \text{CHClBr}_2 \\ 8.94 \end{array}$	$\begin{array}{c} 1.4 \\ \text{CHBr}_3 \\ 9.23 \end{array}$	
$\begin{array}{c} 760 \\ \text{CH}_2\text{Cl}_2 \\ 6.33 \end{array}$	$\begin{array}{c} 26 \\ \text{CH}_2\text{ClBr} \\ 8.42 \end{array}$	$\begin{array}{c} 13.2 \\ \text{CH}_2\text{Br}_2 \\ 8.71 \end{array}$		
$\begin{array}{c} 7100 * \\ \text{CH}_3\text{Cl} \\ 6.19 \end{array}$	$\begin{array}{c} 135 \\ \text{CH}_3\text{Br} \\ 8.19 \end{array}$			

### Discussion of Results.

In view of the polyhalogenated nature of these compounds the possibility of multiple reactions involving substituted radicals could not be ignored. In connection with this it was noticed that some of the compounds ( $\text{CCl}_3\text{Br}$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ ,  $\text{CHBr}_3$  and  $\text{CFBr}_3$ ) showed a faint chemiluminescence in the early experiments with the diffusion flame apparatus, when a high nozzle pressure of sodium and a low concentration of halide were used. These chemiluminescent zones emitted the D line of sodium. It is unlikely that the primary reaction in any of these instances is sufficiently exothermic to excite the D line, since this would necessitate the assumption of improbably low values for the C—Cl and C—Br bond strengths. The luminescence is very probably due to a secondary reaction involving the halogenated radical, the heat of reaction in this case being greater than 48.3 k.cal./mol., e.g.



followed by



The heat change of the latter reaction may be large because it probably includes the energy change of a quadrivalent carbon atom to a divalent carbon atom ( $\sim 37$  k.cal./mol.).<sup>11</sup> When one of this group of halides,  $\text{CHCl}_2\text{Br}$ , was introduced by means of a nozzle into a large excess of sodium vapour in a "highly dilute flame" apparatus,<sup>12</sup> the D line of sodium was strongly emitted and a dark deposit, presumably carbon, was formed on the sides of the reaction vessel. In this case the carbon atom is probably stripped of all its halogen atoms.

If the rate of such a secondary reaction were of the same order, or faster than the corresponding primary reaction, then, in a case where the secondary reaction were occurring to an appreciable extent, the experimental value of the velocity constant would be greater than the true value for the primary reaction. This effect will arise when the value

<sup>11</sup> Norrish, *Trans. Faraday Soc.*, 1934, **30**, 110; Heitler and Hertzberg, *Z. Physik*, 1929, **53**, 52.

<sup>12</sup> M. Polanyi, *Atomic Reactions*, 1932.

of  $P_{\text{Hal}}/P_{\text{Na}}$  is small and will increase as this ratio decreases. Thus, in order to minimise the influence of any secondary reaction in the flame zones the ratio  $P_{\text{Hal}}/P_{\text{Na}}$  was maintained as large as possible in both methods. A comparison of the early results for  $\text{CHBr}_3$ ,  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$  obtained on the diffusion apparatus (when  $P_{\text{Hal}}/P_{\text{Na}} \sim \frac{1}{4}$ ) and those obtained later (when  $P_{\text{Hal}}/P_{\text{Na}} \sim 4$ ) showed that the former values of  $k$  are smaller than the latter as is to be expected when there is an increasing tendency to form core flames at low values of  $P_{\text{Hal}}/P_{\text{Na}}$ ; an increasing preponderance of secondary reaction, on the other hand would be expected to cause an increase in the value of  $k$  for the low values of  $P_{\text{Hal}}/P_{\text{Na}}$ . The authors consider that the above facts indicate that the collision yields given in this paper are determined by the rates of the primary reaction. The discrepancy between the collision yields given by the two methods in certain instances is at the moment unexplained. The discrepancy, however, is not relevant to the main point made here because it does not introduce contrary trends in reaction rates or influence our correlation of these trends with trends in atomic refraction.

The previous results for polychlorinated methane derivatives are shown in Table VI.

The values given in column 4 are those obtained by the diffusion flame

TABLE VI.

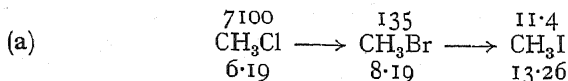
Compound.	Collision Yield. <sup>1</sup>	Collision Yield. <sup>2</sup>	Collision Yield.
$\text{CH}_3\text{Cl}$	10,000	7100	—
$\text{CH}_2\text{Cl}_2$	900	310	760
$\text{CHCl}_3$	100	22	50
$\text{CCl}_4$	25	2	5.5

method in the present investigation. Although our results show appreciable divergencies from the earlier results of Hartel, Meer and Polanyi<sup>1</sup> the gradation of collision yields shown by our results is very close to that shown by the results of Heller and Polanyi.<sup>2</sup> The

actual values of the collision yields are, however, a factor of 2-3 times larger than the corresponding yields given by Heller and Polanyi (col. 3).

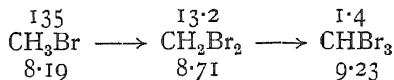
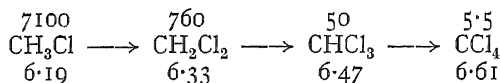
In a review of the diffusion flame method, Heller<sup>3</sup> has concluded that the range of collision yields over which the method can be used with accuracy, is 50-5000. The agreement between the results of the diffusion flame and life period methods in our experiments indicate that with the modified experimental conditions the range of the diffusion flame method can be extended to collision yields as low as ten, and perhaps five. This extension is due to the use of low carrier gas pressures (high values of  $\delta$ ) which enable the ratio of  $P_{\text{Hal}}/P_{\text{Na}}$  to be maintained at substantially high values even for very fast reactions, which would otherwise tend to give "core" flames.

In the schematic presentation of the results (Table V) the triangle for the halides which contain C, H, Br and Cl can be divided into a number of series by taking compounds lying along any particular straight line. The arrows indicate trends of decreasing collision yields, *i.e.* increasing reaction velocity, or increasing atomic refraction per bromine or chlorine atom as explained above. It can be seen that the whole of the results are embraced by the generalisation that an increase in atomic refraction goes parallel to a decrease in collision yields. Particular instances of this are:—

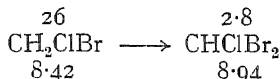


In this case the actual reaction changes along the series; a different halogen atom is removed by the reaction in each case.

(b) In a homogeneous series, *i.e.* only one halogen involved, increase of the number of halogen atoms causes an increase in atomic refraction per halogen atom and a decrease in collision yield, *e.g.*

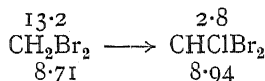
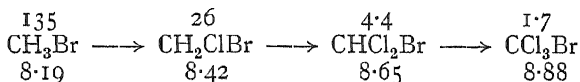


This parallelism has been pointed out previously by one of the authors in the case of the series of chlorides.<sup>3</sup> The same effect is exhibited in the case of mixed halides, *e.g.*

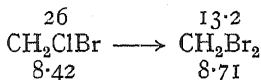
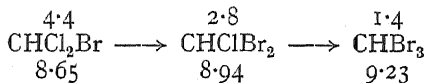
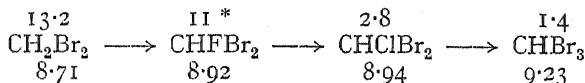


Presumably  $\text{CClBr}_3$  where there is a further increase in the atomic refraction per bromine atom, would react faster than  $\text{CHClBr}_2$ .

(c) In the case of a series of mixed halides each containing bromine increase in the number of chlorine atoms causes an increase in atomic refraction per bromine atom and a decrease in collision yield.



(d) Replacement of H by F, F by Cl, or Cl by Br in a bromide results in an increased atomic refraction per bromine atom and a decreased collision yield, *e.g.*



The parallelism between the decreasing force constant for the C—Cl bonds and the increasing reaction rate, along a series  $\text{CH}_3\text{Cl} \rightarrow \text{CCl}_4$  has already been pointed out.<sup>2</sup> It has also been shown that there is a progressive increase in atomic refraction of the chlorine atoms along this series.<sup>3</sup> Our results show that there is a parallelism between the increase

\* This value is the collision yield given by the Life Period Method.



in reaction rate and atomic refraction which extends over all the polyhalogenated methane derivatives. In the case of the series  $\text{CH}_3\text{Br} \rightarrow \text{CBr}_4$  we have a further instance of a progressive decrease in force constant of the C—Br bond along the series from  $\text{CH}_3\text{Br}$  to  $\text{CBr}_4$ .<sup>5</sup> It seems probable, therefore, that in all these polyhalogenated methane derivatives, increase in atomic refraction or reaction velocity will run parallel to decreasing force constants for the particular C—Hal bonds. Furthermore, it has been pointed out by Sidgwick<sup>13</sup> that there is a small decrease in the C—Cl bond strengths in the series  $\text{CH}_3\text{Cl} \rightarrow \text{CCl}_4$ , the values being 74.7, 72.5 and 72.6 k.cal./mol. for  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  respectively. In view of this it might be concluded that the increases in reaction rate and atomic refraction also run parallel to a decrease in bond strength throughout the whole series of methane derivatives. However, there is, at present, no further bond strength data to confirm such a conclusion.

At the present moment it is not possible to deal with these parallelisms in a quantitative manner with any degree of certainty, and further clarification must await advances in the theoretical methods available for treating reactions involving such polyatomic molecules.

In conclusion, the authors wish to thank Professor Polanyi for much helpful advice during the work, Professor Van Arkel, of Leiden University, for the organic halides, and the D.S.I.R. for a research grant to one of us (J.N.H.).

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<sup>13</sup> Sidgwick, *The Covalent Link in Chemistry*, p. 121.

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## THE THEORY OF THE FORMATION OF PROTECTIVE OXIDE FILMS ON METALS, II.

By N. F. MOTT.

*Received 5th December, 1939.*

### 1. Introduction.

In a recent note<sup>1</sup> the author has suggested a theory to account for the fact that oxide films formed in air at not too high a temperature on such metals as aluminium or chromium reach a thickness of some 50 Å. and then virtually stop growing, unless damaged by cracking or in some other way. The theory started from the assumption, due to Wagner, that metal ions and electrons diffuse through the oxide layer and react with the oxygen at the oxide-gas interface; and it depended on the fact that, according to quantum mechanics, electrons in a metal can penetrate a distance of the order of 50 Å. into an insulating layer *without* receiving energy of excitation; in order to pass through thicker layers they must receive energy from heat motion, so that a kind of thermionic emission occurs from the metal into the oxide. The reaction is thus impossible at low temperatures for layers thicker than 50 Å. The process by which electrons can pass through thin layers is known as the quantum-mechanical tunnel effect, and has been used, for instance, to account for the emission of electrons in strong fields from metals.

<sup>1</sup> Mott, *Trans. Faraday Soc.*, 1939, **35**, 1175; referred to as *loc. cit.*

The aims of this paper are the following :—

(1) To show that the theory given in the paper quoted yields, at any rate for a certain range of thicknesses, a logarithmic law of growth connecting the thickness  $x$  with the time  $t$ ,

$$x = K \log (at + c) \quad (1)$$

where  $K$ ,  $a$  and  $c$  are constants. Such a law gives a negligible rate of growth above a certain thickness, which depends very little on the temperature.

(2) To make more precise the conditions under which the theory can be applied, and to show under what conditions the more familiar parabolic law

$$x^2 = \text{const. } t \quad (2)$$

is to be expected.

(3) To show that under certain conditions the rate of growth given by (2) should fall off for thick films to one given by

$$x^3 = \text{const. } t \quad (3)$$

(4) To apply the theory to the formation of protective films on alloys.

(5) To discuss other processes which may lead to a logarithmic law of growth.

## 2. Mechanisms for the Growth of Oxide Films.

In all the processes considered in this paper, we shall assume that metal ions diffuse through the oxide layer and react with the oxygen at the oxide-oxygen interface. We do not believe that oxygen ions, molecules or atoms diffuse *interstitially* through oxide layers, owing to their large size; oxygen may diffuse through cracks, but such cases will be excluded from the considerations of this paper until the last section.

There are two ways in which the metal ions can move through the oxide layer:

(a) They can be taken into solution at the metal-oxide interface. The oxide near to the metal will then contain an excess of metal, which will be present interstitially. The concentration of metal ions will decrease towards zero as we approach the oxide-gas interface, and the concentration gradient will lead to a flow of metal ions.

(b) The metal is insoluble in the oxide, but the oxide can dissolve oxygen. This, for instance, is the case for the oxidation of copper. Cuprous oxide takes up excess oxygen by leaving vacant lattice positions normally occupied by copper ions. These vacant lattice points are mobile; a copper ion can move into an adjacent vacant lattice position, and another copper ion can then move up and take its place. Thus, although oxygen is dissolved in the oxide, it is actually the copper ions that move. The vacant lattice points formed at the oxide-oxygen interface move inwards until they reach the oxide-metal interface, where they are filled up by metal ions.

Oxidation by process (a) will normally take place when the oxide is a "reduction semi-conductor," *i.e.* a substance whose conductivity is increased by heating *in vacuo*, whereby oxygen is driven off, leaving excess metal atoms in interstitial positions.  $\text{ZnO}$ <sup>2</sup> and  $\text{Al}_2\text{O}_3$ <sup>3</sup> are

<sup>2</sup> Fritsch, *Ann. Physik*, 1935, **22**, 375.

<sup>3</sup> Hartmann, *Z. Physik*, 1936, **102**, 709.

oxides of this type. Process (b) is applicable to oxidation semi-conductors, such as cuprous oxide.

In order that an oxide film shall grow it is necessary that electrons as well as ions shall pass through the oxide layer. This again can take place in various ways:

(i) By thermionic emission from the metal into the "conduction levels" of the oxide. We may denote by  $\phi$  the corresponding work function.  $\phi$  will not of course be equal to the work function of the metal *in vacuo*.<sup>4</sup>

(ii) By the motion of "positive holes" from the oxide-gas interface inwards. What is meant by a "positive hole" may be explained as follows: suppose that an oxygen atom takes its place in the oxide lattice at the surface, next to a metal ion which has just diffused through. Then from an ion on the surface a pair of electrons will be missing. Two electrons from a neighbouring oxide ion could move on to it. The process could be repeated; and the point from which the electrons were missing could diffuse through the oxide layer until finally filled up by electrons from the metal. A lattice point from which electrons are missing is called a "positive hole." In the interior of an oxide layer a positive hole, like an electron in the conduction layer, can move quite

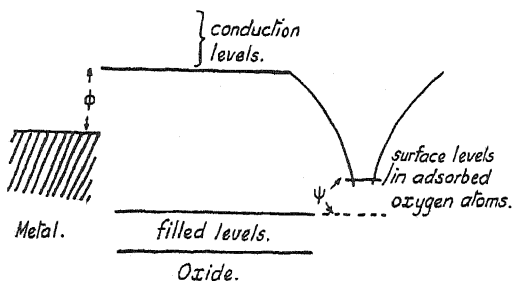


FIG. 1.—Energy levels in metal in contact with oxide layer.

freely without any activation energy. But a certain energy  $\psi$  will be required to move the positive hole away from the surface (cf. Fig. 1):

(iii) As pointed out in our previous paper, electrons can penetrate a *thin* oxide layer (less than about 50 Å.) without receiving the energy  $\phi$  from heat motion, by quantum mechanical tunnel effect. In the same way positive holes could penetrate thin layers.

The rate of growth depends on the number  $j$  of ions crossing unit area per unit time. If  $\Omega$  is the volume of the oxide per metal ion, the rate of growth is given by

$$\frac{dx}{dt} = j\Omega \quad (4)$$

For the moment we shall leave out of consideration the process (iii) above. If we assume that the growth of the film is determined by the diffusion of ions and electrons from the metal to the oxygen-oxide interface, then  $j$  is determined by the following equations (5), (6) and (7).

$$\begin{aligned} j &= -D_i \frac{\partial n_i}{\partial x} + F n_i v_i \quad (5) \\ &= -D_e \frac{\partial n_e}{\partial x} - F n_e v_e \end{aligned}$$

<sup>4</sup> Cf. for instance, Mott, *Trans. Faraday Soc.*, 1938, **34**, 500.

Here  $n_i$ ,  $n_e$  denote the concentrations of ions and electrons at a distance  $x$  from the metal-oxide interface.  $D_i$ ,  $D_e$ ,  $v_i$  and  $v_e$  denote diffusion coefficients and mobilities. The first equation gives the number of ions (assumed singly charged) and the second the equal number of electrons crossing unit area per unit time.  $F$  is the field set up in the oxide which is determined by Laplace's equation

$$\frac{dF}{dx} = 4\pi(n_i - n_e)e \quad (6)$$

Similar equations may be written down when  $n_i$ ,  $n_e$  refer to vacant lattice points or to positive holes.

Unfortunately, general solutions of these equations have not been obtained; we shall confine ourselves to limiting cases.

We may distinguish first between *thin* films, in which the distributions of ions and electrons in the film may be calculated independently of each other, and *thick* films, in which the space charges set up if  $n_i$ ,  $n_e$  are unequal become important. We may estimate the film thickness  $x$  for which the space charges become important as follows: A concentration  $n$  of ions of one sign will give a field, according to (6), having a maximum value  $F = 4\pi n e x$ . If this field is to have a negligible effect in comparison with the concentration gradient, we must have

$$F n v = 4\pi n^2 e v x \ll D \frac{dn}{dx},$$

or, writing  $\partial n / \partial x \sim n/x$  and  $v/D = e/kT$ , we have  $x \ll x_c$ , where

$$x_c = \sqrt{(kT/4\pi n e^2)} \quad (7)$$

Numerical values will be given below.

We consider first, then, the behaviour of *thin* films. We shall discuss explicitly the cases where the ions and electrons pass from the metal to the oxygen-oxide interface. The theory can easily be adapted to apply to the other cases.

We denote as before by  $\phi$  the work required to bring an electron from the metal into the oxide, and by  $W$  the work required to bring a positive ion from the metal to an interstitial position in the oxide. Thus we may distinguish two cases:

**The case where  $\phi < W$ .**—It is then easier to bring electrons than ions into the oxide from the metal. There will thus be a uniform concentration of electrons in the oxide film and a concentration gradient of ions. Thus, the rate of growth is determined by the rate at which ions diffuse through the film—there being an ample supply of electrons. If  $n(x)$  is the number of ions per unit volume at a distance  $x$  from the metal-ion interface, the flow of ions will be given by

$$j = -\frac{\partial n}{\partial x} D_i \quad (8)$$

The equation may be integrated subject to the conditions that  $n = 0$  at the free surface and  $n = n_0$  at the metal oxide interface;  $n_0$  is here the concentration of metal ions in the oxide in equilibrium with the metal, and is given by

$$n_0 = N e^{-W/kT} \quad (9)$$

where  $N$  is the number of interstitial positions per unit volume ( $N \sim 10^{22}$ ).

We thence obtain

$$j = n_0 D_i / x,$$

or from (4),

$$\frac{dx}{dt} = \frac{n_0 \Omega D_i}{x}$$

whence

$$x^2 = A_i t, \quad A_i = 2n_0 \Omega D_i \quad (10)$$

A parabolic law of growth is thus obtained for all thicknesses less than  $x_0$  with a rate constant  $A$  which increases rapidly with temperature.

Numerical estimates of the constants involved may be of interest. We may take  $N\Omega \sim 1$ ,  $D_i \sim 10^{12} \text{ sec.}^{-1} \times (10^{-8} \text{ cm.})^2 e^{-U/kT}$  where  $U$  is an activation energy. Thus

$$A_i \sim 10^{-4} e^{-(W+U)/kT} \text{ cm.}^2/\text{sec.}$$

If one atomic layer is added per day,  $dx/dt \sim 10^{-13}$ , and for a film 10 layers thick  $x \, dx/dt \sim 10^{-20}$ . Thus  $(W+U)/kT \sim 16 \log 10 \sim 37$ . If  $(W+U)/kT$  is much bigger than this, practically no growth is possible.

**The case where  $\phi > W$ .**—There are now more ions in solid solution in the oxide than there are electrons. For very thin films (say less than 20 Å.), however, the electrons will pass through the oxide layer by quantum mechanical tunnel effect as fast as they can be used up the other side to form  $O^{--}$  ions; therefore the rate will be controlled by the rate of diffusion of the metal ions, and hence by (10). For thicker layers, for which the rate of penetration is very slow, the rate of growth will be controlled by the tunnel effect. As shown in our previous paper, this gives a rate of growth

$$\frac{dx}{dt} = K e^{-x/x_0},$$

where  $K$ ,  $x_0$  are constants. This, on integration, gives

$$x = x_0 \log_e \left( \frac{Kt}{x_0} + \text{const.} \right) \quad (11)$$

We obtain thus a logarithmic law of growth.

Finally, when the rate of growth given by (11) has shrunk to very small values indeed, the rate of growth must be determined by thermionic emission of electrons followed by their *diffusion* through the oxide, and hence by an equation of the type (10), only with a much smaller value of  $A$ , since  $n_0$  represents the electronic concentration, proportional to

$$e^{-\phi/kT}.$$

Thus, for very thin films or very thick films (subject to the limit  $x < x_0$ ) we must always expect a parabolic law of growth; but for thicknesses of the order of 30-40 Å. a logarithmic law of the type (11).

It was suggested in our previous paper that, for the oxide films formed on such metals as aluminium, chromium and perhaps zinc at room temperature,  $\phi$  was so great that emission of electrons from the metal to the oxide was practically impossible, at any rate at room temperature. We thus expect for these metals an initial parabolic law of growth, giving way after a few atomic layers have been formed to a logarithmic law. The logarithmic law of growth (11) gives a practically negligible rate of thickening above a certain thickness of the order of 40 Å., and this is just what is observed for those metals on which protective films are formed.

According to our hypothesis, then, the limiting thickness of protective films is due to the difficulty in getting electrons from the metal to the oxide-gas interface, rather than to the difficulty in getting ions through. This hypothesis is fully borne out by the fact that films thicker than 10,000 Å. can be obtained on aluminium by anodic oxidation,<sup>5</sup> which shows that aluminium ions can pass through the layer if oxygen ions are supplied at the free surface.<sup>6</sup>

### 3. Detailed Calculations of Film Growth when $\phi > W$ .

We shall now discuss in greater detail the constants occurring in these equations. We must first examine the parabolic law of growth, for large thicknesses, where the rate is governed by thermionic emission of electrons, in order to see how big  $\phi$  must be for this process not to take place with measurable velocity. This will give a necessary condition for the formation of protective films. The rate is given by (10), namely

$$x^2 = A_e t \quad A_e = 2n_e \Omega D_e,$$

where  $n_e$  is the concentration of electrons in the oxide in equilibrium with the metal. This is given by the vapour pressure formula<sup>7</sup>

$$n_e = \frac{2(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\phi/kT} \\ \sim 10^{19} e^{-\phi/kT} \text{ cm.}^{-3}.$$

The mobility  $v$  of electrons in oxides and other ionic crystals is known experimentally<sup>8</sup> to be of the order 100 cm./sec. per volt/cm. or  $3 \times 10^4$  e.s.u., and to vary comparatively slowly with  $T$ . The diffusion coefficient may be deduced from the equation  $D_e = kTv/e$ ; we obtain  $D_e \sim 0.25 \text{ cm.}^2/\text{sec.}$  With  $\Omega \sim 10^{-22} \text{ cm.}^3$  we see that

$$A_e \sim 5 \times 10^{-4} e^{-\phi/kT} \text{ cm.}^2/\text{sec.}$$

Suppose, then, we have a layer 50 Å. thick, the rate of growth is  $A/2x$  or  $1000e^{-\phi/kT} \text{ cm./sec.}$  The time taken to add each atomic layer is thus of the order  $10^{-9} e^{\phi/kT}$  secs. If this is to be greater than, for instance, a day ( $\sim 10^5$  secs.), we must have

$$\phi/kT > 14 \log_e 10 \sim 33.$$

If no growth is to take place by this process at room temperature ( $kT \sim 0.025 \text{ eV}$ ),  $\phi$  must thus be greater than about 1 eV, a result already obtained by a cruder method in *loc. cit.*

We shall examine next the assumption which gives the logarithmic law of growth (11). The first assumption that we make is that an electron incident on a potential barrier of thickness  $x$  and height  $U$  has a chance of penetration given by the usual quantum mechanical formula<sup>9</sup>

$$P = P_0 \exp \{-4\pi\sqrt{(2mU)x}/h\} \quad . \quad . \quad . \quad (12)$$

$P_0$  is a numerical factor which without sensible error may be put equal to unity. An electron will, however, only be able to penetrate the oxide

<sup>5</sup> Sutton and Willstrop, *J. Inst. Metals*, 1928, 38, 259.

<sup>6</sup> The fact that aluminium will function freely as a cathode is probably due to the presence of cracks in the oxide, which, under cathodic conditions, are not healed up.

<sup>7</sup> R. H. Fowler, *Statistical Mechanics*, 2nd edn., Cambridge (1936), p. 345.

<sup>8</sup> Engelhard, *Ann. Physik*, 1933, 17, 501.

<sup>9</sup> Cf. for example, Dushman, *Elements of Quantum Mechanics*, p. 67.

layer from the metal if there is an oxygen atom the other side ready for it. Now we are assuming that the rate of growth is controlled by the penetration of electrons. Ions will diffuse through the layer and react with oxygen at the surface until the positive charge on the surface prevents further diffusion, until the arrival of the electrons. If  $F$  is the field in the oxide layer, then, if there is to be no flow of ions

$$Fn_i v_i = D_i \frac{\partial n_i}{\partial x}.$$

Putting  $\partial n_i / \partial x \sim n_i / x$  and  $v/D = e/kT$ , this gives

$$F = kT/ex.$$

The density of charge on the surface due to unpaired metal ions is  $F/4\pi$ , and thus the number of such ions per unit area is

$$kT/4\pi e^2 x.$$

This gives approximately the number of oxygen atoms; thus for the proportion of the surface area which can receive an electron we have

$$a^2 kT / 4\pi e^2 x. \quad (13)$$

( $a \sim$  lattice parameter). This is about  $1/3000$  for layers 50 Å. thick.

The probability that an electron incident on the oxide layer should penetrate it is thus given by the product of  $P$  and (13). The number of electrons in the metal with energies between any limits is given by the Fermi-Dirac function. We may deduce that, if  $N$  is the total number of electrons in the metal, the number passing through unit area of the layer per unit time is

$$\frac{kTu^2}{4\pi e^2 x} \frac{3N}{4\pi u_{\max}^3} \int_0^\infty du \int_{-\infty}^\infty dv dw \frac{u \, du \, dv \, dw}{e^{\frac{1}{2}m(u^2+v^2+w^2)/kT} + 1} e^{-4\pi\sqrt{\{2m(\phi - \frac{1}{2}mu^2)\}x}/h}$$

where  $u_{\max}$  is the maximum energy of the electrons in the metal.

The integration may be carried out in ascending powers of  $T$ , and gives per cm.<sup>2</sup> per sec.,  $Me^{-x/x_0}$ , where

$$M = \frac{kTu^2}{4\pi e^2 x} - \frac{6N}{m^2 u_{\max}^3} - \frac{\phi^2 x_0^2}{x^2} \left[ 1 + \frac{\pi^2 x^2 (kT)^2}{24 \phi^2 x_0^2} \dots \right]$$

and

$$x_0 = h/4\pi\sqrt{2m\phi} \quad (14)$$

To obtain the rate of growth  $dx/dt$  we multiply by the molecular volume  $\Omega$ . Thus we obtain the logarithmic law (II) already given, where  $x_0$  is independent of temperature,  $K(=M\Omega)$  increases rather more rapidly than the first power of  $T$ , and also varies slowly with  $x$ .

As regards numerical values, if  $\phi$  is expressed in eV

$$x_0 = 1.2 \times 10^{-8} \phi^{-\frac{1}{2}} \text{ cm.}$$

As we have seen,  $\phi$  must be greater than 1 eV, for protective films to be formed at all, so

$$x_0 < 1.2 \times 10^{-8} \text{ cm.}$$

For films 50 Å. thick we have for  $K$  from formula (14)

$$K \sim 1 \text{ cm./sec.}$$

We may take the limiting film thickness to be that at which one atomic layer is added in a year (say  $10^7$  sec.). Then  $dx/dt \sim 10^{-15}$  and

$$x/x_0 \sim 15 \log_e 10 \sim 35.$$

For  $x_0 = 1.2 \times 10^{-8}$  cm., this gives for the maximum thickness obtainable with any value of  $\phi$  large enough to give protection (viz.,  $\phi \sim 1$  eV),

$$x \sim 44 \times 10^{-8} \text{ cm.}$$

If  $\phi$  were 4 eV, the thickness would be  $22 \times 10^{-8}$  cm.

If we took for our limiting film thickness that for which one atomic layer were added in a day, we should get values of 40 and 20 Å. respectively.

These thicknesses seem, as regards the order of magnitude, to be in good agreement with experiment. L. Tronstad<sup>10</sup> gives the following table for films which have reached a constant thickness:

Mercury in dry air	.	.	.	.	.	.	15-20	Å.
Aluminium in dry air	.	.	.	.	.	.	100-150	Å.
Iron in dry air	.	.	.	.	.	.	15-40	Å.
Austenitic stainless steel	.	.	.	.	.	.	10-30	Å.

In *loc. cit.*, we deduced a thickness of about 100 Å. from measurements of Vernon on the increase of mass of aluminium exposed to air. Dr. Vernon has, however, pointed out to me that if we introduce Erbacher's<sup>11</sup> factor of 2.5 to correct for the ratio of real to apparent surface, we obtain a thickness of 40 Å. in agreement with the theory.

A thickness of 40 Å. for the oxide film formed on aluminium at room temperature after an exposure of a few months has also been found by Steinheil<sup>12</sup> from the progressive increase of transparency of evaporated aluminium films when exposed to air.

In a recent paper Vernon<sup>13</sup> and his co-workers have measured the rate of oxidation of zinc; below 225° C. protective films were formed, and the rate of growth satisfied approximately the equation

$$x = a \log (bt + 1).$$

Since we do not expect the logarithmic law to be valid in the early stages of growth, we cannot compare the constant  $b$  in this equation with the constants of our theory. The constant  $a$ , which determines the limiting thickness, should, however, be very nearly equal to our  $x_0$ . Vernon found between 50° and 225° C. a value of about 0.08 mg./dm.<sup>2</sup>, or assuming a density of unity for the oxygen in ZnO,  $0.8 \times 10^{-8}$  cm., which is the right order of magnitude ( $x_0 = 1.2/\sqrt{\phi} \times 10^{-8}$  cm., according to theory, and  $\phi \lesssim 1$  eV).

#### 4. Protective Films on Alloys.

We have in this section to consider the formation of protective films on such alloys as those of iron with chromium or aluminium.

We have to note in the first place that protective oxide films can be formed at temperatures at which there is no possibility of metallic diffusion within the alloy. Therefore, when an oxide film is formed, both metals must enter into the oxide layer in the same proportion as that in which they are present in the alloy. That the constitution of the metal underneath the protective layer is the same as in the interior of the metal is also borne out by the fact that successive formations

<sup>10</sup> Quoted by Evans, *Metallic Corrosion, Passivity and Protection*, p. 76 London (1937).

<sup>11</sup> *Z. physik. Chemie*, 1933, **63**, 215.

<sup>12</sup> Steinheil, *Ann. Physik*, 1934, **19**, 465.

<sup>13</sup> Vernon, Akeroyd and Stroud, *J. Inst. Metals*, 1939, **6** (advance copy).



and removals of the protective films do not alter the capacity of the metal to form the films.

On the other hand, quite small additions of a second metal are sufficient to give considerable resistance to corrosion (e.g. 7 per cent. of Al in iron,<sup>14</sup> or 3 per cent. of Al in Cu at 800° C.<sup>15</sup>). It is unlikely that 7 per cent. of aluminium in ferrous oxide would be sufficient to alter the work function  $\phi$  of the oxide-iron interface sufficiently to prohibit the passage of electrons. We therefore suggest that initially a mixed oxide is formed, but as the film thickens the part of the film next to the metal becomes rich in aluminium (or chromium in chromium steels) until it becomes impervious to electrons, while an iron oxide film is formed *outside* it. The latter film is without influence on the protective properties.

The way in which this may be expected to happen is the following: so far we have considered the metallic ions as leaving the surface layer of the metal and moving in the oxide from one interstitial position to another until they reach the oxide-oxygen interface. Another process may possibly be occurring at the same time; a metal ion in an interstitial position may change places with a metal ion in the oxide lattice. In an oxide of a single metal this process will not have any observable effect; but in the mixed oxide the divalent ferrous ion will leave its lattice position with the expenditure of *less* energy than the trivalent aluminium or chromium ions. Therefore, in the layers next to the metal the ferrous ions will frequently be replaced by the trivalent ions, while mainly ferrous ions will succeed in penetrating to the surface and forming new oxide layers.

It may be mentioned that Fröhlich,<sup>15</sup> in his investigations of films of the order  $10^{-4}$  to  $10^{-3}$  cm. thick formed on copper and its alloys at 800° C., has found an effect of this type experimentally; he finds that alloying 2 or 3 per cent. of aluminium, beryllium or magnesium with the copper gives a very considerable protection against oxidation, the protective film being formed between the metal and the main oxide layer, and consisting predominantly of the oxide of the alloyed metal.

It should be emphasized that our theory applies primarily to oxidation at low temperatures, at which diffusion of one metal through the other is impossible. At high temperatures, on the other hand, it is possible that the proportions of the two metals in the oxide layer may be different from their proportions in the alloy. That this is the case is suggested by experiments of Iitaka and Miyake,<sup>16</sup> who find that the protective films formed on copper-beryllium alloys containing 1 per cent. of beryllium heated to a red heat give the electron diffraction rings characteristic of BeO alone. In order to explain these results we may assume that diffusion within the metal takes place readily, and also that the beryllium ions diffuse through the oxide layer much faster than the larger copper ions, so that a protective film of BeO is formed before any appreciable amount of  $\text{Cu}_2\text{O}$  appears.

## 5. Thick Films.

So far we have considered films so thin that the space charge set up by the diffusing ions and electrons is negligible. The critical thickness,

<sup>14</sup> Portevin, Pretet and Jolivet, *J. Iron Steel Inst.*, 1934, **130**, 219.

<sup>15</sup> K. W. Fröhlich, *Z. Metallkunde*, 1936, **28**, 368.

<sup>16</sup> *Nature*, 1936, **137**, 457.

if given by (7), which may be written

$$x_c = \sqrt{(kT \Omega D / \pi e^2 A)}$$

where  $A$  is the constant in the growth equation. For a film that grows to  $10^{-4}$  cm. in an hour,  $A \sim 10^{-5}$ , and, if the growth is governed by the diffusion of electrons,  $D \sim 0.2$  cm.<sup>2</sup>/sec. Putting in numerical values, we obtain

$$x_c \sim 3 \times 10^{-5} \text{ cm.}$$

If the rate of growth is controlled by the rate of diffusion of positive ions,  $D$  and hence  $x_c$  will be smaller.

We consider, then, the limiting case of films thick compared with  $x_c$ .

If the film when of stoichiometric composition is a conductor (e.g. an ionic conductor, as are silver halides above room temperature), then no space charges can be set up, and the laws of growth are the same as for thin films. For insulators, however, since we must have no large space charge set up, we may assume that the concentration of ions and electrons is equal, except in the oxide film at a distance comparable with  $x_c$  from the metal. Moreover, the constant  $n_0$  which occurs in equation (10) in the formula for  $A$  will no longer be  $Ne^{-\psi/kT}$ ,  $Ne^{-W/kT}$ , whichever is the smaller, but  $Ne^{-\frac{1}{2}(\phi+W)/kT}$ . Thus, unless  $\phi$  and  $W$  happen to be exactly equal, the value of  $A$  appropriate to thick films is greater than for thin films. We thus expect

$$x^2 = At \quad (\text{thin films})$$

$$\frac{dx}{dt} = \frac{A^1}{2x}, \quad x^2 = A^1(t + t_0) \quad (\text{thick films})$$

with

$$A^1 > A.$$

The plot of  $x^2$  against  $t$  should thus be as in Fig. 3.

There is, however, one case in which thick films should grow more slowly than thin ones. Suppose that metal ions go into interstitial positions in the oxide, but electrons are not transferred through the conduction band of the oxide, but as positive holes through the full band. This will be the case if, in Fig. 1,  $\psi < \phi$ . Then the diffusing particles, positive ions and positive holes, will both produce a positive space charge in the oxide.

It follows that the concentration  $n$  of neither electrons nor ions can reach a value great enough to set up a field large enough to stop the diffusion of either. Since the field is proportional to  $n_0 x$ , we deduce that  $n_0$  near a boundary, instead of remaining constant as the film thickens, decreases as  $1/x$ . Thus the equation governing the growth will be of the form

$$\frac{dx}{dt} = \frac{\text{const.}}{x^2}$$

or  $x^3 = at + b$ .

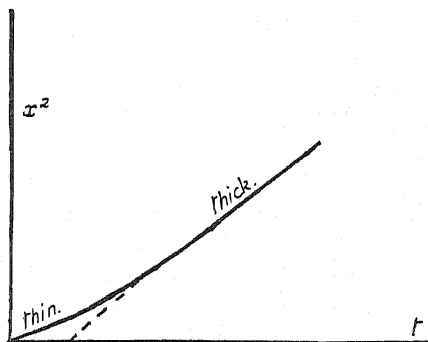


FIG. 2.—Theoretical growth law for insulating oxides.

At present we do not know of any reaction to which these considerations are applicable.

### 6. A Logarithmic Law of Growth due to Recrystallisation.

Some metals, *e.g.* copper, form compact oxide films of any thickness, the rate of growth following the parabolic law. These films give interference colours at suitable thicknesses. No interference colours are obtained with the protective films on aluminium or chromium, probably because they are not thick enough. There is a third type of oxide film, such as that formed on zinc<sup>13</sup> above 225° C., which follows a logarithmic law of growth, but reaches much greater thicknesses ( $\sim 500$  Å.) than the protective films, and whose growth rate is very sensitive to temperature. These films do not give interference colours, and show a granular structure under the microscope. It is suggested that in these cases the original compact film breaks up and recrystallises, a hypothesis confirmed by electron diffraction results due to Shearer.<sup>17</sup>

It may be worth while to state a set of assumptions applicable to these thicker films from which a logarithmic law can be derived. Before recrystallisation we imagine a thin film (Fig. 3(a)), during recrystallisation we imagine that the metal is covered by a number of islands of oxide, as in Fig. 3(b). We assume that at any part of the surface which is not already covered there is a probability  $p$  per sec. per cm.<sup>2</sup> that an island will begin to form, and that once started it will grow rapidly to a weight  $w$ , which we assume to be independent of the presence of neighbouring islands. We also assume that each island

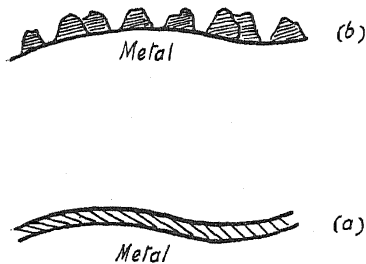


FIG. 3.

- (a) Compact film before recrystallisation.  
(b) Film after recrystallisation.

will cover an area  $a$ , some of which may, however, already be covered by other islands.

Considering unit area of surface, the probability that a given point is covered by a given island is  $a$ ; therefore the probability that it is *not* covered is  $(1 - a)$ . If there are  $n$  islands per unit area, the fraction of the surface which is not covered is thus

$$(1 - a)^n.$$

The number of islands formed per second is thus  $p(1 - a)^n$ , so that if  $W$  is the mass of oxide per unit area,

$$\frac{dW}{dt} = pw(1 - a)^n.$$

But  $W = nw$ , so this equation becomes

$$\begin{aligned} \frac{dW}{dt} &= pw(1 - a)^{W/w} \\ &\sim pwe^{-Wa/w}, \end{aligned}$$

<sup>17</sup> Unpublished; quoted by Vernon, *e.a. loc. cit.*

since  $a$  is small,  $W/w$  large. Integrating this, we obtain

$$W = \frac{w}{a} \log (pat + 1),$$

which is the required equation.

The author would like to express his thanks to Dr. W. H. J. Vernon for valuable discussions of the experimental material.

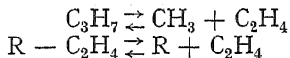
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## THE POLYMERISATION OF ETHYLENE BY ALKYL RADICALS.

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Polymerisation reactions have long attracted attention by reason both of their scientific interest and their industrial importance. Most of these reactions, however, hardly admit of a complete theoretical treatment. In fact, the different stages in polymerisation, *viz.* formation of active centres or nuclei, development and breaking of the chain, etc., cannot be adequately explained by experimental data alone, but need also the postulation of certain hypotheses usually difficult to verify. Thus, the active centres are often supposed to be activated molecules or bivalent radicals, the existence of which has not been proved by independent methods. Again, the question whether it is the activation energy, or the steric factor that plays an important part in the progress and stopping of the chain, is still open to discussion. Finally, the reaction products are, in most cases, complex mixtures or polymers not easy to analyse. The complexity, therefore, of the question, while rendering futile any attempt at formulating a general solution to all the problems raised in polymerisation, suggests, at the same time, a delimitation of the field of investigation to one of the many groups and sub-groups into which polymerisation reactions may be conveniently divided, and the choice from it of one particular case for theoretical treatment. We selected for our study the polymerisation of ethylene by radicals for a two-fold reason. First, because ethylene appears to be the unit in the building-up of radicals and molecules, from the fact that complex molecules decompose, under certain experimental conditions, into simple ones and ethylene, while simple radicals add up with ethylene to give complex ones, thus pointing to the existence of an equilibrium of the type

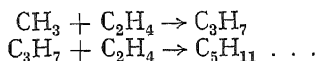


Secondly, because ethylene polymerisation, for the reason just given, offers a very good means of studying the inter-relations between different radicals from the point of view of polymerisation efficiency.

Previous researches have shown that polymerisation could be induced by free radicals from acetone, azo-methane, mercury-dimethyl, etc.<sup>1</sup>

<sup>1</sup> See *e.g.*, Taylor and Jungers, *Trans. Faraday Soc.*, 1937, **33**, 1353.

More recently, Joris and Jungers<sup>2</sup> polymerised ethylene with ethyl radicals produced from ethyl iodide in the presence of mercury. The alkyl iodides exhibit in the ultra-violet an absorption band with a maximum at about 2600 Å. corresponding to the dissociation of the molecule into a radical and an atom of iodine. The technique devised in the case of ethyl iodide permits, therefore, of the production of alkyl radicals for study under comparable conditions. The radicals studied in the present research are methyl, ethyl, *n*- and *iso*-propyl. Since the mechanism proposed for ethylene polymerisation is a succession of bimolecular additive reactions,



it should be possible to verify it with the help of the above series of radicals in which the first and last members differ by a molecule of ethylene. Also, valuable information may be obtained concerning the variation of steric factor and activation energy in the course of the reaction, and the mechanism of the chain breaking.

### 1. Experimental Procedure.

The methyl and *n*-propyl iodides used were Merck's, the ethyl and *iso*-propyl, Fraenkel's products. The apparatus was, in principle, the same as that of Joris and Jungers.<sup>2</sup> Alkyl iodides, after being freed from all volatile impurities, were introduced into adequate vessels and were kept, when not actually in use, in liquid air to avoid decomposition or contamination by foreign products. Mixtures of ethylene and iodide, in varying proportions, could be introduced into the reaction chamber consisting of a silica tube of 3 cm. in diameter and 20 cm. in length and fitted inside with a pyrex tube having small receptacles for the mercury what is necessary to take up the iodine liberated from the alkyl iodides during the reaction. The upper end of the chamber was connected with a side tube terminating in a small bulb in which gaseous reaction products could be condensed with freezing mixtures of known temperature and analysed for methane and hydrogen. To maintain the reaction chamber at any desired temperature, it was enclosed in a cylindrical electrical furnace of thick aluminium wound round with resistance wire and provided with an aperture closed with a quartz tube permitting the entrance of light.

The source of light was a mercury arc of the Heraeus type operated at high temperature at 110 v. and 3.5 amp., the distance from the centre of the arc to that of the reaction vessel being 14 cm. For certain experiments, voltage and distance were changed to 150 v. and 10.5 cm., and 75 v. and 22 cm. respectively, the amperage remaining constant, in order to secure varying light intensities. The light was filtered through uviol glass before entering the reaction vessel.

Pressure variations were measured manometrically at room temperature. Any non-volatile products deposited on the walls of the silica vessel were burnt away at the end of the reaction at a dull red heat with a blow-pipe.

### 2. Experimental Results.

Several series of measurements were made so as to compare the efficiencies of radicals under different experimental conditions. The results are recorded in Table I. Column 1 represents the serial number of the experiment; 2, the radical under consideration; 3, 4, 5, respectively, pressure of iodide, of ethylene and pressure variation  $\Delta P$  resulting from the reaction; 6, the yield, *i.e.* ratio between total pressure variation and iodide pressure

<sup>2</sup> Joris and Jungers, *Bull. Soc. Chim. Belg.*, 1938, **47**, 135.

$\Delta P/P_1$ ; 7, the time of half-reaction; 8, remarks. The results are also represented graphically by plotting decrease of pressure against time. In all the experiments, the reaction was followed to completion, *i.e.* till no further

TABLE I.

No. of Experiment.	Radical.	$P$ iodide in cm.	$P$ ethylene in cm.	$\Delta P$ in cm.	$\Delta P/P_1$ .	$t_{\frac{1}{2}}$ Reaction.	Remarks.
<b>A.—Influence of Iodide Pressure and B, of Temperature.</b>							
<b>245° C.</b>							
1	$\text{CH}_3$	6.50	11.83	10.3	1.59	17'	0.45 ( $\text{CH}_4$ )
2	$\text{C}_2\text{H}_5$	6.50	12.03	10.1	1.54	16'	
7	$\text{CH}_3$	2.92	12.23	6.00	2.03	15'	0.12 ( $\text{CH}_4$ )
8	$\text{C}_2\text{H}_5$	2.90	11.70	4.90	1.69	11'	
9	$\text{C}_3\text{H}_7$ (i)	3.17	12.03	2.97	0.95	6'	
3	$\text{CH}_3$	1.75	12.08	3.71	2.12	13'	0.06 ( $\text{CH}_4$ )
4	$\text{C}_2\text{H}_5$	1.60	12.10	2.80	1.75	8'	
5	$\text{C}_3\text{H}_7$ (n)	1.90	12.15	2.28	1.20	7'	
6	$\text{C}_3\text{H}_7$ (i)	1.95	12.15	2.00	1.02	5'	
<b>200° C.</b>							
10	$\text{CH}_3$	3.03	12.42	6.90	2.30	31'	
11	$\text{C}_2\text{H}_5$	3.11	12.07	5.98	1.92	26'	
12	$\text{C}_3\text{H}_7$ (i)	2.97	12.03	4.00	1.35	16'	
16	$\text{CH}_3$	1.89	12.41	4.60	2.44	32'	< 0.01 ( $\text{CH}_4$ )
17	$\text{C}_2\text{H}_5$	2.00	12.20	4.00	2.00	25'	
18	$\text{C}_3\text{H}_7$ (n)	1.80	12.15	3.40	1.89	22'	
19	$\text{C}_3\text{H}_7$ (i)	2.15	12.42	2.89	1.42	13'	
<b>130° C.</b>							
20	$\text{CH}_3$	1.90	12.65	4.75	2.50	$\sim 275'$	
26	$\text{C}_3\text{H}_7$ (n)	2.03	12.15	3.88	1.90	$\sim 235'$	
21	$\text{C}_3\text{H}_7$ (i)	2.05	12.20	2.75	1.34	80'	
<b>C.—Influence of Light Intensity.</b>							
<b>245° C.</b>							
7	$\text{CH}_3$	2.92	12.23	6.00	2.03	15'	I
14	$\text{CH}_3$	3.08	12.20	7.33	2.38	50'	III
9	$\text{C}_3\text{H}_7$ (i)	3.17	12.03	2.97	0.95	6'	I
13	$\text{C}_3\text{H}_7$ (i)	2.95	12.02	3.02	1.02	14'	III
<b>200° C.</b>							
12	$\text{C}_3\text{H}_7$ (i)	2.97	12.03	4.00	1.35	16'	I
15	$\text{C}_3\text{H}_7$ (i)	3.02	12.03	3.82	1.26	10'	II
<b>D.—Influence of Ethylene Pressure.</b>							
<b>200° C.</b>							
24	$\text{CH}_3$	2.10	6.20	3.52	1.67	33'	
25	$\text{C}_3\text{H}_7$ (n)	1.78	6.82	2.68	1.50	27'	
16	$\text{CH}_3$	1.89	12.41	4.60	2.44	32'	
18	$\text{C}_3\text{H}_7$ (n)	1.80	12.15	3.40	1.89	22'	
22	$\text{CH}_3$	2.03	24.75	6.90	3.40	32'	
23	$\text{C}_3\text{H}_7$ (n)	2.00	26.70	4.95	2.47	29'	

pressure variation took place. It is, therefore, from experimentally observed changes of pressure that the yields have been calculated. Yields have been chosen to evaluate the polymerisation efficiencies of radicals,

as they eliminate the factor of the slight pressure variations unavoidable in a series of experiments.

### A. Influence of Iodide Pressure.

The effects produced on polymerisation yields by variations in iodide pressure, at an approximately constant pressure of ethylene, have been studied. The experimental data are recorded in Table I A and B, and

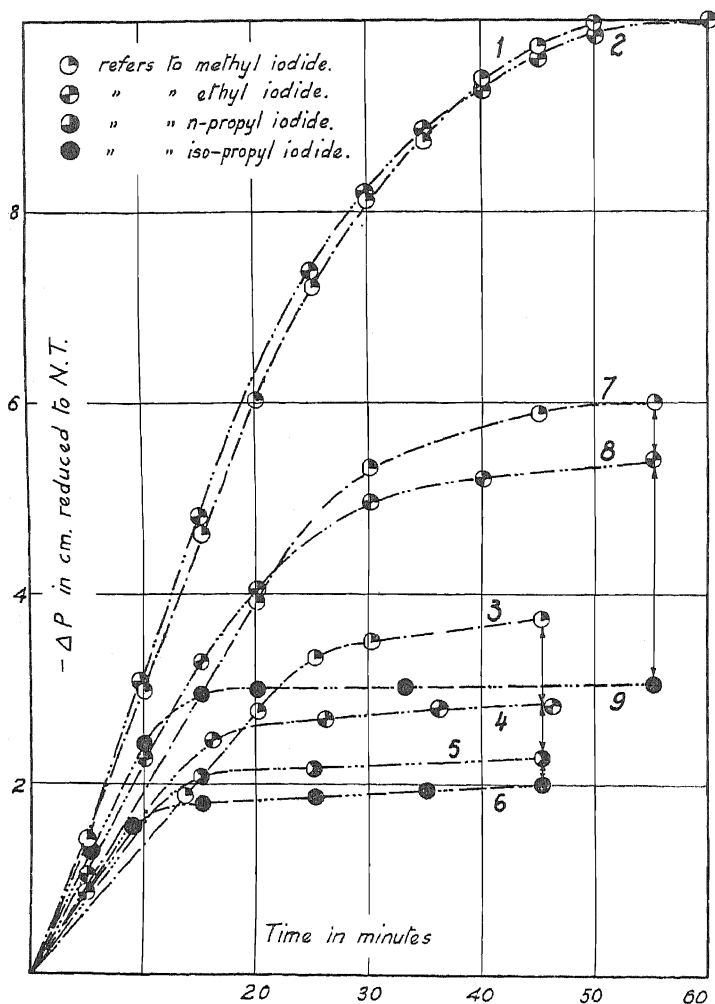


FIG. 1a—Polymerisation of Ethylene at 245° C.

represented by Figs. 1 a, b, c, from which the following conclusions may be drawn. The yield, at a given pressure, decreases down the series of iodides methyl, ethyl, *n*- and *iso*-propyl. This is to be ascribed to the difference in the steric factors of these radicals, as will be explained in detail in the discussion. Secondly, for any radical, the yield increases with decreasing iodide pressure. This may be explained in the following manner. The radicals can react not only with ethylene molecules present but also among themselves, and since this latter reaction increases in importance at higher

radical concentrations brought about by higher iodide pressures whilst the ethylene radical reaction decreases, the polymerisation yield decreases at higher iodide pressures. At lower iodide pressures, on the contrary, the mutual radical combination is favoured less than the main ethylene polymerisation reaction; the more so as the relative concentration of ethylene becomes proportionately greater, and consequently the yield increases. In agreement with this the yield undergoes a further increase when the relative pressure of ethylene is raised still more as in the experiments recorded in Table I D. Finally, the relative differences in yields for the several iodides increase with decreasing iodide pressure, and tend to limiting values at low pressure, near about 2 cm., as may be seen in the case of methyl and ethyl iodides at 245° C. This limiting region of iodide pressure

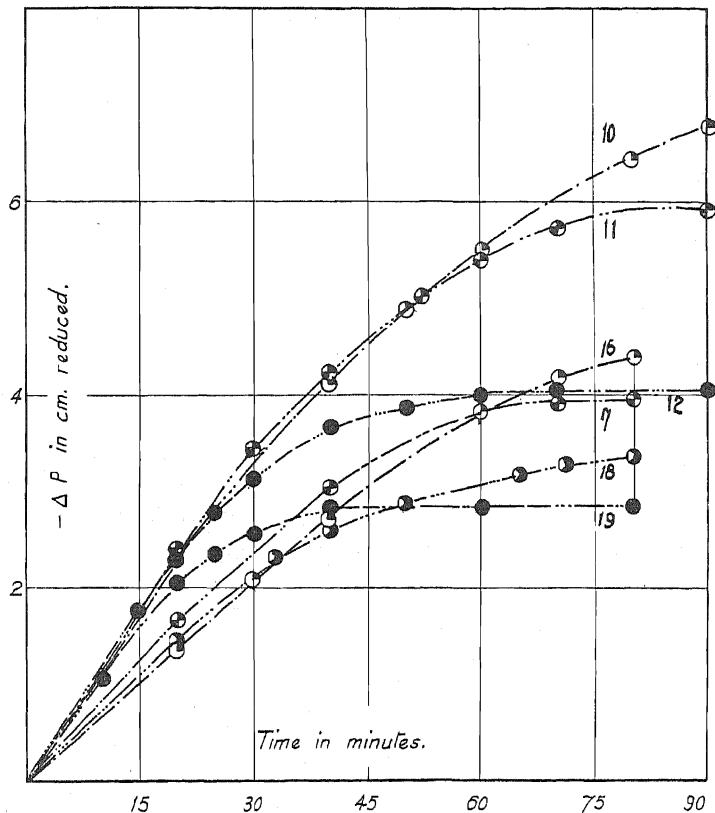


FIG. 10.—Polymerisation of Ethylene at 200° C.

is of particular importance for the study of the specific influence of the individual radicals in the polymerisation of ethylene, because since they are at such a low pressure, in very dilute concentrations, they undergo much less mutual combination and contribute more effectively to polymerisation, each furnishing its characteristic yield. For this reason, experiments were carried out in that iodide pressure region with increasing ethylene pressures, the results of which will be given later.

Here it should be added that only in the case of methyl iodide is there evidence of formation of methane, becoming appreciable at higher iodide pressures and temperatures (see column 7 of Table I A, B), although it is, even under these conditions, negligible with what was obtained by Taylor and Jungers<sup>1</sup> when using acetone as sensitizer.



### B. Influence of Temperature.

Experiments made at 245, 200 and 130° C. show that the behaviour of radicals just described is little modified by temperature variation, except that the yield for all of them increases slightly with lowering temperature. The reason for this is that the radical concentration is slightly smaller at lower temperature due to a lower rate of iodide decomposition and, as was pointed out in the preceding section, a lower radical concentration favours the yield.

### C. Influence of Light Intensity.

To examine the influence of light intensity on yields, experiments were conducted with varying intensities by modifying the voltage and the distance of the arc from the reaction vessel: (I) 110 v., 14 cm.; (II) 150 v., 10.5 cm.; (III) 75 v., 22 cm., amperage in all cases being practically constant. Though the light intensity in each case was not quantitatively determined, a fair idea of it may be gathered from the slopes of the curves

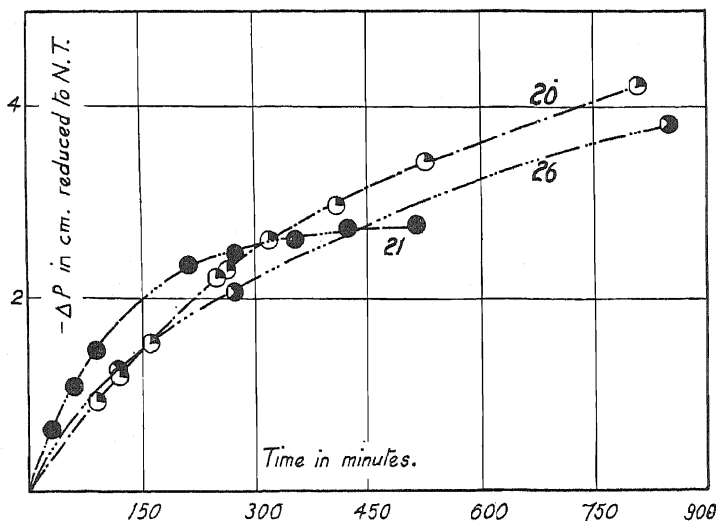


FIG. 1c.—Polymerisation of Ethylene at 130° C.

in Fig. 2. Change of conditions from (I) to (III) produces a clear change in the yields for methyl and *iso*-propyl radicals (Table I C). Lower light intensity, therefore, increases the yield for all the radicals, without at the same time masking the characteristic yield differences existing between the several radicals. This increase with decreasing intensity may be explained in terms of a lower radical concentration, as in the preceding sections.

### D. Influence of Ethylene Pressure.

In the acetone photosensitised polymerisation of ethylene, Taylor and Jungers<sup>1</sup> observed that the yield increased with ethylene pressure and that at a constant acetone pressure of 1.3 cm. it reached a limiting value when ethylene was about 25 cm. pressure. With a view to studying the behaviour of our radicals up to this limiting pressure of ethylene, experiments were made with methyl and *n*-propyl iodides at that iodide pressure at which, as mentioned in sec. 2A, the relative yield differences for radicals were tending to a limit, *viz.* at about 2 cm. pressure. From the experimental data in Table I D, it is obvious that the yields for both radicals

increase with ethylene pressure, and in the neighbourhood of 25 cm. ethylene pressure, the yield for the methyl is 3.4 and for the *n*-propyl radical 2.47, the difference being nearly unity. This means that the methyl radical has been able to add on one ethylene molecule more than *n*-propyl;

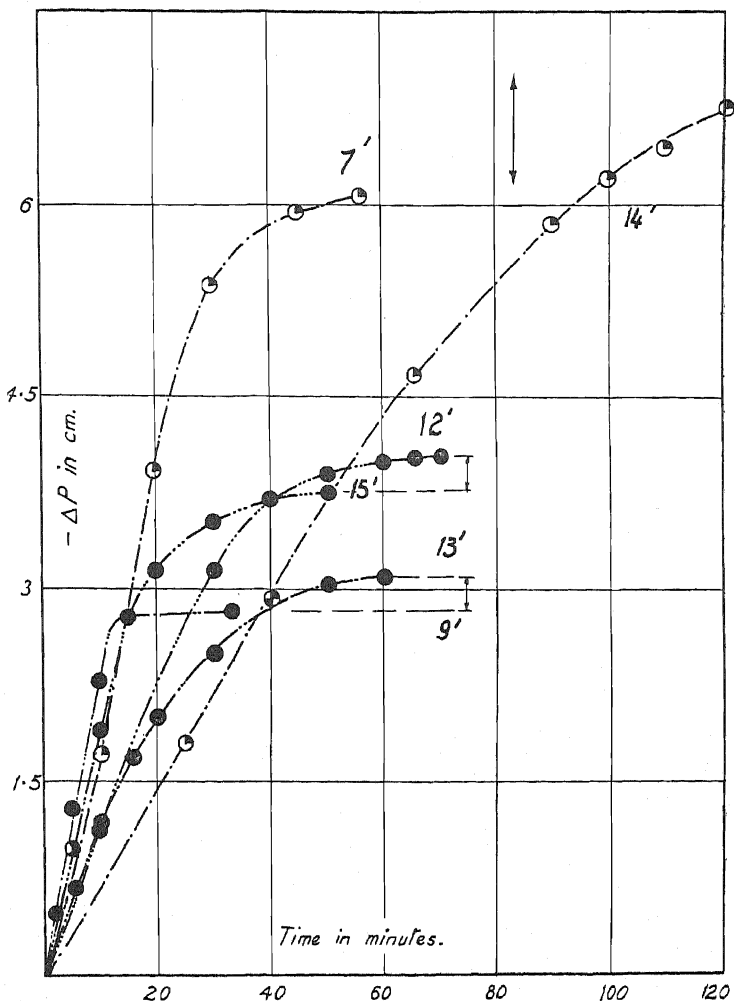


FIG. 2.—Influence of light intensity on the polymerisation yield.

but the fact that the two radicals differ in structure also by one ethylene molecule, leads us to believe that the polymer in either case is similar in form and results from a direct addition of ethylene molecules to radicals.

### 3. General Discussion.

The discussion may be divided into three sections dealing with (a) the primary process of light absorption by alkyl iodides, (b) the formation of the polymer, (c) the mechanism of disappearance of radicals.

**(a) The Primary Process.**

Since the photodecomposition of alkyl iodides provides the radicals necessary for the subsequent polymerisation reaction, interesting information about it may be secured by treating it separately, even though it takes place in our experiments in the presence of ethylene. The primary process in the absorption of light by alkyl iodide is known to be the rupture of the C—I bond, liberating the radical.<sup>3</sup> Due to the occurrence, under ordinary conditions, of the reverse reaction, *i.e.* recombination of the radical and iodine atom, the apparent iodide decomposition is very low.<sup>4</sup> In order to increase this, Joris and Jungers<sup>2</sup> carried out the decomposition in the presence of mercury which takes up the liberated iodine partly to an extent depending on its own vapour pressure at the experimental temperature.



Now Porret and Goodeve<sup>5</sup> have shown that the absorption coefficient, *i.e.* the number of light quanta absorbed per sec., is the same for the iodides in question, so that equal pressures should, for a given light intensity, furnish the same number of radicals per sec. Experiment, however, shows that the time of half-reaction decreases down the series of iodides methyl, ethyl, *n*- and *iso*-propyl (*cf.* Table I A, B). This difference in time cannot be accounted for by the presence of mercury, whose influence is the same for all the iodides. Nor can a satisfactory explanation be given in terms of ethylene, since a four-fold increase of its pressure does not appreciably affect the half-reaction time for methyl and *n*-propyl iodides, as may be seen from the results in Table I D. On the other hand, since the iodide decomposition appears to be the rate determining process, the observed difference must be ascribed to the iodide regenerating step (2) which competes with mercury for iodine, thus partially opposing the decomposition step (1). Now the rate of the back-reaction (2) is faster in the case of the methyl than in that of the ethyl radical, because the former owing to its larger steric factor (*see sec. 3B*) reacts with iodine faster than the latter, and consequently, an apparently slower decomposition rate is observed for methyl than for ethyl iodide. The same explanation holds good for the whole series of iodides, as the steric factor decreases with the complexity of each member of the series.

**(b) Polymer Formation.**

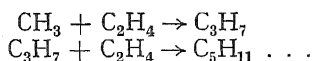
In the sections 2 A and B, it was shown that with decreasing iodide pressures the polymerisation yields for the several radicals and their relative differences increased at first and then, at about 2 cm. pressure, tended to limiting values due to the progressive suppression of mutual radical combination in favour of the main ethylene polymerisation. In section 2D, the yields for methyl and *n*-propyl iodides at a pressure of

<sup>3</sup> (a) Herzberg and Scheibe, *Z. physik. Chem.*, 1930, **7**, 390; (b) Porret and Goodeve, *Trans. Faraday Soc.*, 1937, **33**, 690.

<sup>4</sup> (a) Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689; (b) Spence and Wild, *Proc. Leeds Phil. Soc.*, 1935, **3**, 141; (c) Iredale and Daphne Stephan, *Trans. Faraday Soc.*, 1937, **33**, 800.

<sup>5</sup> Porret and Goodeve, *Proc. Roy. Soc.*, 1938, **31**, 165.

2 cm. with an ethylene pressure gradually increasing up to its own limit of 25 cm. were discussed. In all these limiting cases, the yields differ for methyl and ethyl radicals by values tending to 0.5, and for methyl and *n*-propyl by unity. On the other hand, the radicals themselves differ from one another in structure by half an ethylene molecule  $\text{CH}_2$ . These facts lead us to believe that the polymer in the case of all the radicals is similar in form, and that it may be regarded as being formed by successive additions of ethylene molecules to radicals through bimolecular reactions of the type



the velocity constant of each of these successive steps being given by the general formula

$$k_n = p_n \cdot z_n e^{-E_n/RT}$$

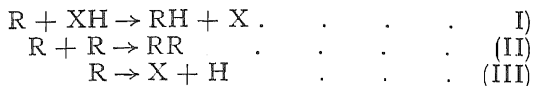
where  $ze^{-E/RT}$  represents the number of collisions with sufficient energy to bring about reaction, and  $p$  is a factor accounting for the fact that not all collisions with the required energy lead to reaction. If the velocity constant  $k$  for any one of these successive steps is very small, it means that that particular step will take place with extreme difficulty, and the step following it will practically not take place at all. Now the fact that the yields for all the radicals are limited to a value  $n$ , as we just remarked, shows ethylene is added up to the  $n^{\text{th}}$  step inclusively of the above series, and not beyond it, because for the  $(n+1)^{\text{th}}$  step  $k_{n+1}$  is almost zero. The reason for this may be sought in the variables  $p$ ,  $E$  and  $Z$ . The changes of  $Z$  with each successive step are much too small compared to its absolute value to account for the vanishing value of  $k_{n+1}$ . If a high activation energy  $E_{n+1}$  were necessary for the  $(n+1)^{\text{th}}$  step to take place an increase in temperature should bring it about and thus increase the yield. But the fact that the yield is approximately the same, despite an increase of temperature from 130 to 245° C., excludes  $E$  from primary responsibility for the above state of affairs. On the contrary, the steric factor  $p$ , whose theoretical significance has been explained by Bawn,<sup>6</sup> is known to decrease markedly with complexity of the radical and to reduce correspondingly its reactivity in association reactions of the type we are concerned with. It is, therefore, the steric factor which largely affects and accounts for the limiting step of the above series of addition of ethylene to radicals.

It may be added that the steric factor for *iso*-propyl radical is smaller than that for *n*-propyl, due to the more complex structure of the former, and consequently the polymerisation yield for the *iso*-radical is slightly lower. This shows that the *n*- and *iso*-radicals when free do not lose their individuality but reveal the influence of their structural differences in polymerisation.

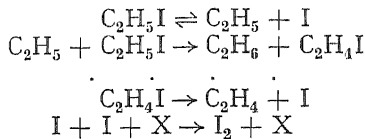
### (c) Disappearance of Radicals.

Regarding the disappearance of radicals, which we have several times mentioned here, three mechanisms may be envisaged, (I) saturation by capture of an hydrogen atom from a neighbouring molecule, (II) bimolecular combination of radicals among themselves, and (III) dissociation into an hydrogen atom and an olefine molecule.

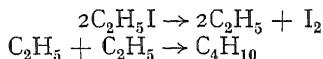
<sup>6</sup> Bawn, *Trans. Faraday Soc.*, 1936, **32**, 178.



According to mechanism (I) as established by West and his co-workers <sup>7</sup> for ethyl iodide decomposition, the reaction scheme will be



and the reaction will take place without affecting the pressure of the system. Mechanism (II) will give, as end-products, dimers of the radical and reduce the pressure, at the end of the reaction, to half its initial value.



This mechanism, involving bimolecular combination, will become less important at low radical concentrations, or not take place at all, in which case the radicals may disappear through mechanism (I). In favour of both these mechanisms we cite the work of Joris and Jungers <sup>2</sup> who found that the photodecomposition of ethyl iodide in presence of mercury (when the radical concentration was high), took place with a pressure variation, and in the absence of mercury, without pressure variation. A similar observation was made by Van Tassel, <sup>8</sup> also in this laboratory, studying the same reaction thermally. It is no doubt to the exclusive occurrence of mechanism (I) that the end-products, ethane and ethylene obtained by West and Ginsburg <sup>7</sup> in ethyl iodide decomposition, and propane and propylene by Glass and Hinshelwood, <sup>9</sup> and Jones and Ogg <sup>10</sup> in propyl iodide decomposition, are to be attributed. In the mercury photosensitised hydrogenation of ethylene, where radical combination must have been appreciable, Jungers and Taylor <sup>11</sup> got almost exclusively butane due to the occurrence of mechanism (II).

Our results do not confirm mechanism (III), *i.e.* dissociation of the radical into an atom of hydrogen and olefine, which has been frequently suggested by several authors, since we do not find even traces of hydrogen in the reaction products.

Consequently, we suggest that in our case mechanism (I) and (II) are both responsible for the disappearance of radicals, the former at low, the latter at high, and both together at intermediate radical concentrations. Further experiments are in progress to analyse completely the products of decomposition of, and the products resulting from the polymerisation induced by alkyl iodides containing upwards of five carbon atoms, in order to throw more light on the proposed mechanisms.

The authors wish to express their thanks to Professor H. S. Taylor of Princeton University for opportunity afforded to discuss certain problems raised in this paper.

<sup>7</sup> West and Ginsburg, *J. Amer. Chem. Soc.*, 1934, **56**, 2626; West and Schlesinger, *J. Amer. Chem. Soc.*, 1938, **60**, 961.

<sup>8</sup> Van Tassel, *Natuurwet. Tydschrift*, 1938, **20**, 83.

<sup>9</sup> Glass and Hinshelwood, *J. Chem. Soc.*, 1929, 1817.

<sup>10</sup> Jones and Ogg, *J. Amer. Chem. Soc.*, 1937, **59**, 1931.

<sup>11</sup> Jungers and Taylor, *J. Chem. Physics*, 1938, **6**, 325.

### Summary.

1. The polymerisation of ethylene by alkyl radicals has been examined. The yield for any one radical increases with increasing ethylene pressure, decreasing iodide pressure and light intensity. For the radicals taken together, it decreases down the series methyl, ethyl, *n*- and *iso*-propyl.

2. The polymer is formed by bimolecular additions of ethylene molecules to radicals. The differences in the photodecomposition rates of the alkyl iodides and their polymerisation yield differences are explained in terms of steric factor.

3. The structural differences between *n*- and *iso*-propyl iodides are clearly revealed both in their photodecomposition rates and polymerisation yields.

4. Two mechanisms account for the disappearance of radicals in this polymerisation, *i.e.* saturation through capture of an hydrogen atom and bimolecular recombination of radicals.

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## THE SURFACE TENSIONS OF METHYL ACETATE SOLUTIONS.

By J. W. BELTON.

*Received 23rd November, 1939.*

There appear to be no accurate data available for the surface tensions of aqueous solutions of methyl acetate—those quoted in the International Critical Tables, for example, are only given to within 2 %. Measurements were therefore made on mixtures of water and redistilled methyl acetate by the maximum bubble pressure method, but using the procedure previously described by the writer,<sup>1</sup> it was found impossible to obtain reproducible results, although no difficulty had been experienced with other organic liquids.<sup>2</sup> By taking suitable precautions, however, it was finally found possible to obtain values with a maximum error of 0.3 %.

The experimental cell was modified by sealing into the side wall (Fig. 1, ref. <sup>1</sup>), a piece of platinum wire bent at right angles and sharpened so that its point was about 0.5 cm. above the jet. The surface of the liquid under observation was altered by a finely adjustable pressure head so that it was coincident with the platinum point when observed with the cathetometer telescope. The measured maximum bubble pressure must be corrected by the head of liquid between the jet and the point; this correction involves the density of the solution and the (directly measured) distance between jet and point, also given by measurements of the maximum bubble pressure for water with its surface at the jet and then with its surface at the point (the position of the jet relative to the point was constant for all determinations).

Some difficulty was experienced in obtaining a uniform, slow rate of bubbles (about 1 per 10 sec.). The pressure tended to mount to a value greater than that for the maximum bubble pressure and then to be released

<sup>1</sup> Belton, *Trans. Faraday Soc.*, 1935, **31**, 1413.

<sup>2</sup> *Ibid.*, 1642.

in a burst of five or six bubbles. By careful adjustment of the pressure, however, a uniform rate was obtained, but only below the maximum concentration recorded below; above this value the bubbles appeared in batches at irregular intervals, with consequent oscillation in the manometer and irreproducibility of results.

Attempts were made to measure the surface tensions by the capillary rise method. The jet was replaced by a capillary tube; the liquid was kept at a fixed level by means of the platinum point, and the pressure necessary to depress the meniscus inside to that outside was measured with the aid of the cathetometer telescope. The results agreed with the bubble pressure method, but for the more concentrated solutions which had given previous trouble, it was not found possible to keep the levels inside and out the same. The failure of the two methods for the stronger solutions is probably linked with the high volatility of methyl acetate.

The methyl acetate used in these experiments had been carefully purified by the method of Young and Thomas,<sup>3</sup> allowed to stand repeatedly over phosphorus pentoxide (which removes both water and alcohol) and distilled. Its density at 25° C. was 0.9296 g./c.c. The water used was distilled from quartz and was stored in a quartz vessel. All measurements were made at 25° C.

### Methyl Acetate-Water Mixtures.

The measured surface tensions are given in Table I, in which  $h$  is the maximum bubble pressure in cms. of butyl phthalate and the concentrations are expressed as mole fractions of methyl acetate. The plot of  $\gamma - N_{\text{MeAc}}$  gives a smooth curve which becomes less steep as the concentration of methyl acetate increases. The vapour pressures of methyl acetate solutions have been determined by McKeown and Stowell,<sup>4</sup> and the plot of their data shows that over the concentration range investigated here Henry's law is obeyed. Assuming that the surface

TABLE I.

$N_{\text{MeAc.}}$	$h.$	$\gamma.$
0.00161	13.525	72.01
0.00321	12.83	66.33
0.00567	11.87	62.92
0.00904	11.235	58.22
		55.08

excess of water is zero, that of methyl acetate may then be calculated from

$$d\gamma = - \Gamma_{\text{MeAc}} RT d \ln N_{\text{MeAc}}. \quad (1)$$

These are given in moles/sq. cm. for rounded concentrations in Table II.

TABLE II.

$N_{\text{MeAc}}$	0.001	0.002	0.003	0.004	0.005	0.006	0.0075
$\Gamma \times 10^{10}$	0.58	0.81	1.16	1.41	1.58	1.27	1.25

The maximum surface excess which occurs at a concentration of methyl acetate of  $N_{\text{MeAc}} = 0.005$  corresponds to an area per molecule of 105 Å<sup>2</sup>. The value of  $\Gamma$  calculated here is that according to the convention of Gibbs, but for low concentrations it is approximately the same as that based on a comparison of equal volumes of liquid.<sup>5</sup> The area per molecule calculated for the total number of molecules in the

<sup>3</sup> Young and Thomas, *J. Chem. Soc.*, 1893, 63, 1191.

<sup>4</sup> McKeown and Stowell, *ibid.*, 1907, 97.

<sup>5</sup> Guggenheim and Adam, *Proc. Roy. Soc., A*, 1933, 139, 227.

surface is then  $79 \text{ \AA}^2$ ; and the corresponding figure for a concentration of methyl acetate of  $N_{\text{MeAc}} = 0.001$  is  $220 \text{ \AA}^2$ . The area per molecule for insoluble long chain esters is given by Adam as  $22 \text{ \AA}^2$ . There is thus ample space for the methyl acetate to be accommodated in the surface layer.

### Methyl Acetate-Water-Sucrose Mixtures.

The influence of sucrose on the adsorption of methyl acetate is of interest. The surface tensions of a series of methyl acetate-water-sucrose mixtures in which the methyl acetate content was kept constant while water and sucrose were added in equimolar quantities, were measured by the method described above. The surface tension increased with sucrose concentration and decreased with that of methyl acetate. This is similar to the effect of both these substances on pure water. The results are given in Table III, which gives the number of moles of methyl acetate, the mole fraction of each component, the maximum bubble pressure, the surface tension and the surface excesses of methyl acetate ( $\Gamma_1$ ) and of water ( $\Gamma_2$ ).

These surface excesses were calculated from the Gibbs equation, in which it has been assumed that the activities of the components may be replaced by their mole fractions. This procedure is partly justified by the data of McKeown and Stowell;<sup>4</sup> the partial pressure of methyl acetate is proportional to its mole fraction and that of water nearly proportional over the concentration range investigated here. We have then

$$d\gamma = -\Gamma_1 RT d \ln N_1 - \Gamma_2 RT d \ln N_2 \quad (2)$$

TABLE III.

$N_1$ .	$N_2$ .	$N_3$ .	$h$ .	$\gamma$ .	$\Gamma_1 \times 10^{10}$ .	$\Gamma_2 \times 10^{10}$ .
$m_1 = 0.00446$ .						
0.001604	0.004962	0.9935	13.59	66.65	1.9	28.6
0.001590	0.009800	0.9890	13.69	67.14		
0.001574	0.01455	0.9840	13.78	67.60		
0.001559	0.01922	0.9793	13.87	68.05		
0.001544	0.02379	0.9745	13.905	68.20		
$m_1 = 0.00892$ .						
0.003223	0.004984	0.9915	12.895	63.25	2.6	20.3
0.003193	0.009842	0.9870	12.99	63.75		
0.003161	0.01462	0.9823	13.03	63.90		
0.003132	0.01931	0.9777	13.07	64.09		
0.003095	0.02385	0.9730	13.165	64.57		
$m_1 = 0.01581$ .						
0.005758	0.005023	0.9890	11.94	58.56	4.3	16.8
0.005705	0.009917	0.9845	12.015	58.92		
0.005646	0.01472	0.9795	12.055	59.13		
0.005594	0.01945	0.9750	12.145	59.55		
0.005539	0.02407	0.9703	12.27	60.17		

where  $N_1$  and  $N_3$  are the mole fractions of methyl acetate and water respectively; the surface excess of sucrose has been put equal to zero. This expression may be differentiated with respect to  $m_1$  and  $m_2$ , the



number of moles of methyl acetate and sucrose present, and we obtain

$$-\frac{1}{RT}\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = -(\Gamma_1 + \Gamma_3)\left(\frac{\partial \ln N}{\partial m_1}\right)_{m_2} + \frac{\Gamma_1}{m_1} + \Gamma_3\left(\frac{\partial \ln m_3}{\partial m_1}\right)_{m_2} \quad (3)$$

and

$$-\frac{1}{RT}\left(\frac{\partial \gamma}{\partial m_2}\right)_{m_1} = -(\Gamma_1 + \Gamma_3)\left(\frac{\partial \ln N}{\partial m_2}\right)_{m_1} + \Gamma_3\left(\frac{\partial \ln m_3}{\partial m_2}\right)_{m_1} \quad (4)$$

where  $N$  is the total number of moles present, which has been taken as constant for a series, although it does vary, but by no more than 2 %. All the slopes involved may be calculated from the data, and the values of  $\Gamma_1$  and of  $\Gamma_2$  evaluated.

Both methyl acetate and water are positively adsorbed at the surface in constant amounts for each series (actually  $\Gamma_1$  shows a decrease and  $\Gamma_3$  an increase of about 2 % in each series with increasing sucrose content). The effect of sucrose is to increase the amount of methyl acetate in the surface, but the extent of the increase is independent of the amount of sucrose present. The amount of water adsorbed is also constant, and is approximately independent of the amount of sucrose, although for aqueous sucrose solutions the adsorption of water varies from about 29 to 17  $10^{-10}$  moles/sq. cm. for the same range of sucrose concentration. As the methyl acetate adsorption increases with increasing methyl acetate content, that of water is reduced, which suggests that water is pushed out of the surface layer and methyl acetate comes in to take its place.

### Summary.

The surface tensions of aqueous methyl acetate solutions have been measured to within 0.3 %, and the surface adsorptions calculated. The effect of the addition of sucrose has been investigated, and it is found that the amount of methyl acetate in the surface is increased, but that the increase is independent of the amount of sucrose added; the amount of water adsorbed is also shown to be independent of the amount of sucrose.

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## MONOLAYERS OF A LONG CHAIN ESTER SULPHATE.

BY EINAR STENHAGEN.\*

*Received 17th January, 1940.*

The strong water affinity of the  $-\text{O}-\text{SO}_3'$  group makes it necessary to attach a very long hydrocarbon chain to it in order to obtain an insoluble monolayer on water. With a chain containing 22 carbon atoms insoluble monolayers, presenting some interesting features, are obtained.

\* Rockefeller Foundation Fellow, 1938-39.

### Experimental.

The measurements were carried out using a Langmuir-Adam trough and a polonium electrode in the usual manner.<sup>1</sup> The potentials were measured with a Lindemann electrometer.

The spreading of the sodium docosyl sulphate presented some difficulty as the sulphate does not dissolve in non-polar organic solvents. Ethyl alcohol was therefore used as solvent, but as this is completely water miscible and the sulphate group is very hydrophilic, 20-50 % of the material spread is lost into the substrate. On leaving the film under no pressure for two hours about 95 % of the amount spread is found in the surface. Once a monolayer is formed, it is very stable and shows no detectable tendency to dissolve.

### Properties of $C_{22}$ Ester Sulphate Monolayers.

Fig. 1 shows the results obtained with the sulphate spread on M/25 phosphate buffer (Clark and Lubs),  $pH$  7.2 and 0.01 N. HCl respectively.

Due to the loss of material during the process of spreading the force-area curves in Fig. 1 have been plotted assuming that the area of the molecule just before collapse at about 65 dynes pressure is  $18.5 \text{ \AA}^2$ . This is the smallest possible area to which a hydrocarbon chain in a monolayer can be compressed before the monolayer collapses (compare Dervichian<sup>2</sup>) and it is reasonable to assume that the area of the  $C_{22}$  ester sulphate at the collapse point has reached this value. The projections of the very slightly compressible high pressure

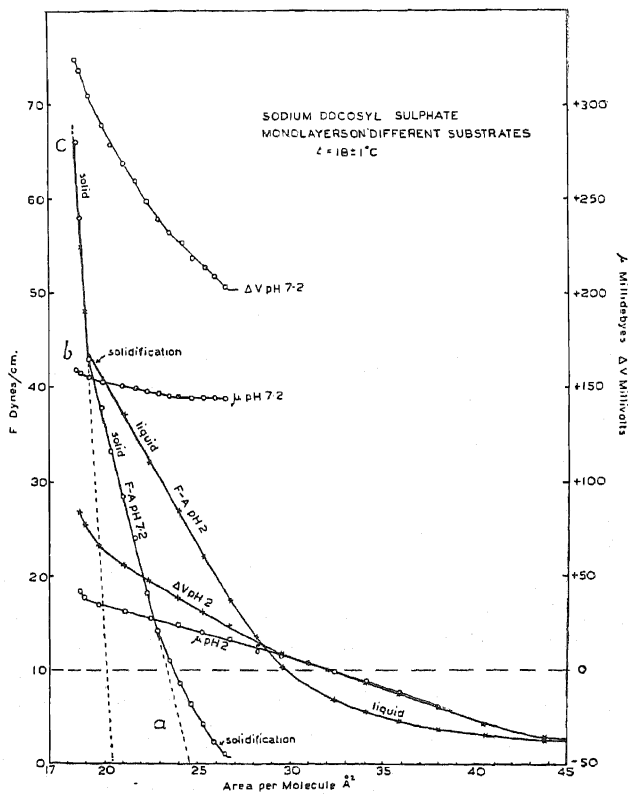


FIG. 1.

region *b-c* on both *F-A* curves in Fig. 1 cut the axis at an area of about  $20.5 \text{ \AA}^2$  which is the same as the mean value,  $20.5 \text{ \AA}^2$ , found by Adam<sup>3</sup>

<sup>1</sup> J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., A*, 1931, **130**, 259.

<sup>2</sup> D. G. Dervichian, *Thèses*, Paris 1936, Masson et Cie.

<sup>3</sup> N. K. Adam, *The physics and chemistry of surfaces*, 2nd edition, Oxford, 1938, p. 48.

for a large number of long chain compounds. At  $pH$  7.2, the projection of the straight part of the F-A curve between 13 and 43 dynes cuts the axis at about  $24.5 \text{ \AA}^2$ . This area (Adam's "area of zero compression")<sup>3</sup> is  $24 \text{ \AA}^2$  for the  $C_{22}$  fatty acid on 0.01 N. HCl and the F-A curve for the  $C_{22}$  sulphate on phosphate substrate at neutral  $pH$  therefore resembles the curves obtained with carboxylic acids in the undissociated form. The pressure values are considerably higher, however, and it is necessary to apply more than 40 dynes pressure before the incompressible region  $b-c$  is reached (about 24 dynes in case of carboxylic acids). The monolayer is extremely stable and can be left for several minutes at 60 dynes without appreciable fall in pressure. The monolayer is already solid at a pressure of 3 dynes at an area of  $26 \text{ \AA}^2$ . The surface potential  $\Delta V$  and the corresponding surface moment  $\mu$  are low. The potential is uniform to 4 millivolts and  $\mu$  is nearly constant at about 150 millidebyes, slowly rising on compression of the monolayer. There is a distinct small rise in the high pressure region above 40 dynes.

On 0.01 N. hydrochloric acid (Fig. 1,  $pH$  2) the monolayers are expanded. On compression solidification of the monolayer does not occur until the incompressible region is reached above 40 dynes/cm. The surface potential is negative at large areas, passes through zero and is then rising. As on neutral substrate, there is a distinct rise in the region  $b-c$  (Fig. 1). Above  $45 \text{ \AA}^2$  the potential fluctuates somewhat and remains at about  $-40 \text{ mV}$ . out to  $55 \text{ \AA}^2$ .

On pure distilled water and on 0.01 N. NaOH the same type of curve is obtained as on the neutral phosphate buffer. In both cases the monolayer solidifies at 2-4 dynes pressure. The surface potential is somewhat lower than on the phosphate buffer with its higher salt concentration. In view of the ester nature of the sulphate extreme acid or alkaline substrates have not been used.

$Ba^{++}$  in a concentration of 0.001 N. (neutral substrate) does not affect the F-A curve, the condensing effect of  $Ba^{++}$  and  $Ca^{++}$  found for carboxylic acids being entirely absent. This must be attributed to the fact that barium salts of ester sulphates are water soluble, *i.e.*, the presence of  $Ba^{++}$  does not affect the ionisation and hydration of the ester sulphate head group.

Attempts to build multilayers, using the Langmuir-Blodgett technique, were not successful, the chromium slide coming out wet from all substrates tried. This shows only that the ester sulphate is very hydrophilic.

### Discussion.

The fact that the monolayer on neutral and alkaline substrates solidifies even at a pressure of a few dynes and an area per molecule of about  $26 \text{ \AA}^2$ , indicates a strong interaction between the (hydrated) sulphate head groups in the ionised state. At  $pH$  2, when the head group dissociation is diminished this interaction is decreased and the monolayer is expanded and does not solidify on compression until the high pressure region  $b-c$  is reached, *i.e.*, not until the chains are closely packed. The pressure needed to reach this point probably represents the work needed to dehydrate and reorientate the head group. In general, monolayers are expanded or gaseous when the head groups are fully dissociated, as shown by carboxylic acids on very alkaline solutions<sup>4</sup> and primary amines on acid solutions. In the case of the former the partly dissociated state in the neutral  $pH$  range makes the monolayers condensed, due to ion-dipole interaction. The behaviour

<sup>4</sup> N. K. Adam and J. Miller, *Proc. Roy. Soc., A*, 1933, 142, 401.

of the sulphate is contrary to this general behaviour as the ionised monolayer is solid at a few dynes pressure and an area of 26 Å.<sup>2</sup>

Very long hydrocarbon chains tend to make the films solid, but the nature of the head group is still more important, for instance, pyridinium bromide, with a 22 carbon chain forms gaseous films.<sup>5</sup> Long chain ureas<sup>6</sup> below a certain temperature are solid at 26 Å. The urea differs from the sulphate in that the monolayer is extremely incompressible whereas the latter can be compressed to the area occupied by the closely packed chain.

The vertical component of the dipole moment of the complicated head group decreases on decreasing ionisation, which can be compared with that of fatty acids which increases under the same condition and that of primary amines, which is fairly constant irrespective of the degree of ionisation.

In the case of carboxylic acids, the decrease in  $\mu$  is attributed<sup>7</sup> to the introduction of an additional dipole on ionisation, consisting of the positive ion below and the negative oxygen above, which neutralises the dipole present in the fatty acid. For the sulphate, this would require that the positive ion had an average position above the negatively charged oxygen. This, however, is somewhat difficult to conceive and it is perhaps more probable that the change in potential is due to some reorientation of the head group on ionisation.

The symmetrical tetrahedral arrangement of the oxygen atoms around the sulphur atom explains the very low surface potential of the unionised sulphate.

It is very uncommon in an insoluble monolayer for the surface potential to change sign on compression, which occurs with the sulphate on 0.01 N. HCl substrate; but it has been observed, for instance, with adsorbed layers of sodium benzoate.<sup>8</sup> When the surface concentration is increased, the potential changes from negative to positive, as in the case of the sulphate.

The author is indebted to Professor E. K. Rideal for his interest and advice, and to Dr. T. Malkin, Bristol, for a very pure specimen of sodium docosyl sulphate.

### Summary.

The properties of monolayers of sodium docosyl sulphate on different substrates are described and discussed.

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<sup>5</sup> Adam, *l.c.* <sup>3</sup>, p. 129.

<sup>6</sup> *Ibid.*, p. 55.

<sup>7</sup> *Ibid.*, p. 72.

<sup>8</sup> Frumkin, *cf.* Adam, *l.c.* <sup>3</sup>, p. 136.

# THE CONVERSION OF PARAHYDROGEN BY PORPHYRIN COMPOUNDS, INCLUDING HEMOGLOBIN.

By D. D. ELEY.

Received 9th January, 1940.

The conversion of *parahydrogen* by paramagnetic gases, and by paramagnetic gases and ions in solution, was discovered by Farkas and Sachsse.<sup>1, 2</sup> A theoretical treatment by Wigner<sup>3</sup> showed that under the influence of an inhomogeneous magnetic field a *parahydrogen* molecule exhibits an observable probability for the para-ortho transition, the calculated collision efficiency of  $10^{-12}$  to  $10^{-14}$  agreeing with experiment. Such a mechanism is also considered to account for the conversion at low temperatures on many heterogeneous catalysts, such as charcoal,<sup>4, 5</sup> and metals, metallic oxides and salts.<sup>6</sup> The conversion on those catalysts which are diamagnetic is attributed to a surface paramagnetism. We have examined a number of compounds of the porphyrin type, both as heterogeneous catalysts and in solution, which might be expected to be free from such complications, and find that the paramagnetic compounds show a conversion of the kind discussed. The absence of any true activation of hydrogen is not unexpected, since in biochemical systems the heme compounds appear to be usually associated with an activation of oxygen through the ferric-ferrous change.<sup>7</sup> Some experiments on the closely related structures, metal-free phthalocyanine and copper phthalocyanine, are included.

## Experimental.

All experiments were made under static conditions. The heterogeneous catalysts were examined in glass vessels of 150 c.c., which could be evacuated to  $10^{-6}$  mm., and which were connected to a system consisting of manometers, storage bulbs for the gases used, and the thermoconductivity apparatus. The solutions were placed in a 100 c.c. vessel, which was attached to the apparatus by a flexible glass spiral tube, so that it could be shaken at 4 to 5 vibrations per second. The *para* H<sub>2</sub> and total D-content analyses were made, on small samples withdrawn from the reaction vessel by the method of Farkas,<sup>8</sup> and the H<sub>2</sub> + D<sub>2</sub> = 2HD analyses by the method of Melville and Bolland.<sup>9</sup>

The blood corpuscles, obtained by centrifuging ox-blood, were washed with Ringer's solution, and suspended in this solution for an experiment. The hematin was the brown amorphous powder supplied by B. D. H. The hemin consisted of well-formed crystals prepared according to Gattermann's *Laboratory Methods of Organic Chemistry*, 1932, page 395.

<sup>1</sup> Farkas and Sachsse, *Z. physikal. Chemie B*, 1933, **23**, 1.

<sup>2</sup> *Ibid.*, 19.

<sup>3</sup> Wigner, *ibid.*, 28.

<sup>4</sup> Bonhoeffer, Farkas and Rummel, *ibid.*, **21**, 225.

<sup>5</sup> Rummel, *ibid.*, **167**, 221.

<sup>6</sup> Taylor and Diamond, *J. Amer. Chem. Soc.*, 1935, **57**, 125.

<sup>7</sup> Warburg, *Biochem. Z.*, 1924, **152**, 479.

<sup>8</sup> Farkas, *Z. physikal. Chemie B*, 1933, **22**, 344; Eley and Tuck, *Trans. Faraday Soc.*, 1936, **32**, 1425.

<sup>9</sup> Melville and Bolland, *ibid.*, 1937, **33**, 1316.

The hematoporphyrin was obtained from Dr. Theodore Schuchardt. The metal-free phthalocyanine and copper phthalocyanine were kindly supplied by Professor R. P. Linstead; a second sample of copper phthalocyanine was prepared by twice extracting with quinoline a sample of I.C.I. "Monastral fast blue" powder, previously baked out *in vacuo* for 30 hours at 300° C. The hydrogens were purified by palladium.

### Heterogeneous Conversion.

In this paper conversions are expressed by the constant  $k = 1/t \ln C_0/C_t$ , where  $C_0$  is the effective concentration of parahydrogen at the beginning of the experiment (*i.e.* excess over the equilibrium value) and  $C_t$  is the effective concentration at time  $t$ . In agreement with earlier work, this equation was found applicable for all the heterogeneous and dissolved catalysts examined. Care was taken to outgas all catalysts at temperatures well below those at which decomposition starts. Table I. shows that at room temperature and lower temperatures a conversion is catalysed by the paramagnetic solids, but not by the diamagnetic solids. It also shows an absence of any  $H_2 + D_2$  reaction, in the case of the heme compounds at the maximum working temperature. These

TABLE I.

Catalyst.	$\mu$ , Bohr Magnetons.	T° C.	$p$ mm.	$t$ Hours.	$k$ Hours <sup>-1</sup> .
Hematoporphyrin . . . . .	0.0 <sup>a</sup>				
100 mg. . . . .		22	14 $pH_2$	24	—
200 mg. . . . .		100	100 $H_2D_2$	288	—
Hematin . . . . .	5.6 <sup>b</sup>	20	65 $pH_2$	17.3	0.036
200 mg. . . . .		20	6 $pH_2$	3.1	0.039
				6.0	0.036
				9.0	0.036
				22.0	0.035
		20	0.8	3.1	0.038
400 mg. . . . .		20	16 $pH_2$	23.8	0.075
		100	40 $H_2D_2$	480	—
Hemin 100 mg. . . . .	5.8 <sup>b</sup>	185	20 $pH_2$	—	0.012
		20	20 $pH_2$	—	0.011
700 mg. . . . .		120	40 $H_2D_2$	288	—
		121	33 $pH_2$	17.7	0.066
		-80	30 $pH_2$	3.5	0.063
Metal-free Phthalocyanine					
150 mg. . . . .	0.0 <sup>c</sup>	-80	27 $pH_2$	63	—
Copper Phthalocyanine					
390 mg. . . . .	1.7 <sup>d</sup>	-80	21 $pH_2$	16.2	0.004
400 mg. . . . .		-80	40 $pH_2$	—	0.003
		20	40 $pH_2$	—	0.001
4.4 g. (from Monastral blue) . . . . .		20	30 $H_2D_2$	144	—
		-80	28 $pH_2$	3.2	0.186
		0	26	16.9	0.082
		20	23	24.0	0.021
		20	23	23.0	0.023
		112	27	16.5	0.014

<sup>a</sup> Inferred from measurements on related porphyrins, by Haurowitz and Kittel, *Ber.*, 1933, 66, 1046.

<sup>b</sup> Pauling and Coryell, *Proc. Nat. Acad. Sci.*, 1936, 22, 159.

<sup>c</sup> Lonsdale, *J.C.S.*, 1938, 364.

<sup>d</sup> Klemm and Klemm, *J. prakt. Chemie*, 1935, 143, 82.

data establish the conversions as of the paramagnetic type. At 200°–300° C. an  $H_2 + D_2$  reaction has been observed on a number of phthalocyanines, but since this property would appear to involve some activation of the catalyst,<sup>10</sup> we are not concerned with it here.

In Table I. and Fig. 1 we give some data on the kinetics, showing the applicability of  $k$  and its independence of pressure. For hematin and copper phthalocyanine the temperature coefficients are negative, corresponding respectively to apparent activation energies of –1300 and about –2300 cal. This behaviour is similar to that previously observed, and from the published constants at two temperatures for charcoal, Ni, Cu and NaCl in the low temperature region we estimate

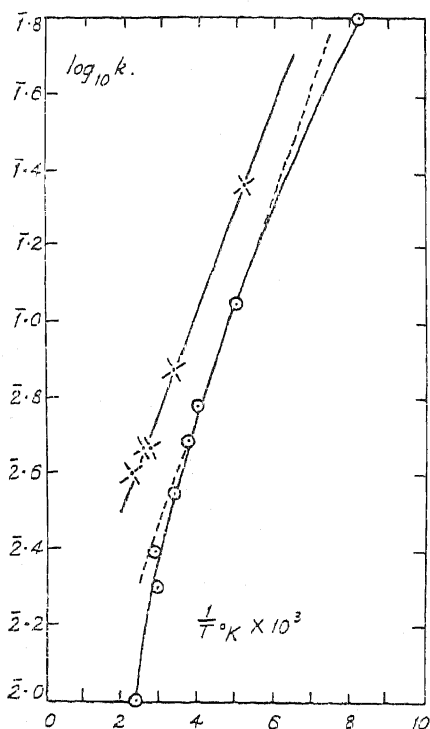


FIG. 1.—Parahydrogen conversion on Solid Hematin. (X 0.04g. specimen. O 0.02g. specimen.)

apparent activation energies of –400 to –1600 cal. Bonhoeffer, Farkas and Rummel consider that on charcoal the reaction of the  $H_2$  molecules in the adsorbed layer proceeds with zero true activation energy, and the apparent activation energy is to be associated with the heat of Van der Waal's adsorption of  $H_2$  on the catalysts. That such is not necessarily the case is shown by the data for hemin, where  $k$  is independent of temperature over –80° C. to 180° C.; the absence of any  $H_2 + D_2$  reaction rules out the possibility that the catalyst is in the intermediate range between low and high temperature mechanisms such as was observed for charcoal. Such an independence of temperature would be observed if every molecule during its stay in the adsorption layer were converted, when the reaction velocity would be given by the number desorbing per second. If we approximate the adsorbed layer as a two-dimensional gas, then the desorption velocity is equal to the classical number of collisions with the surface.<sup>11</sup> From a microscopic measurement of the average size of crystal, we roughly attribute to the hemin a surface of 100 cm.<sup>2</sup> per 100 mg. Such a quantity of hemin converts  $3.0 \times 10^{14}$  molecules of *para*  $H_2$  per second at 20° C. and 20 mm. pressure. Since the collision number is  $2.9 \times 10^{24}$  molecules sec.<sup>-1</sup>, it is clear that desorption is not the rate-determining step, and in fact the collision yield of  $10^{-10}$  is similar in order to that found for gaseous  $O_2$  as catalyst, where it is about  $10^{-12}$ .<sup>1</sup> We are inclined to attribute the behaviour of hemin to the fact that an actual activation energy is

<sup>10</sup> Polanyi, *Trans. Faraday Soc.*, 1938, 34, 1191.

<sup>11</sup> Kimball, *J. Chem. Physics*, 1938, 6, 447.

required for reaction in the adsorption layer, in magnitude fortuitously equal to the energy of adsorption. Such an energy might well be required to bring the  $H_2$  molecule sufficiently close to the magnetic centre for the ordinary transition probability to be reached. A similar activation might be expected for the paramagnetic ions, where a partial penetration of the hydration shell is considered necessary.<sup>12, 13</sup> The temperature coefficients of these reactions have not been measured, however. The structures of hemin and hematin being so analogous, it is difficult to see *a priori* why they should show this difference in behaviour, which might indeed be a function of the mode of preparation (only one hemin preparation was examined). Even if this is so, the significance of the observation stands, and a detailed investigation of the temperature coefficients of conversion and of the adsorption will be necessary to clear up the matter.

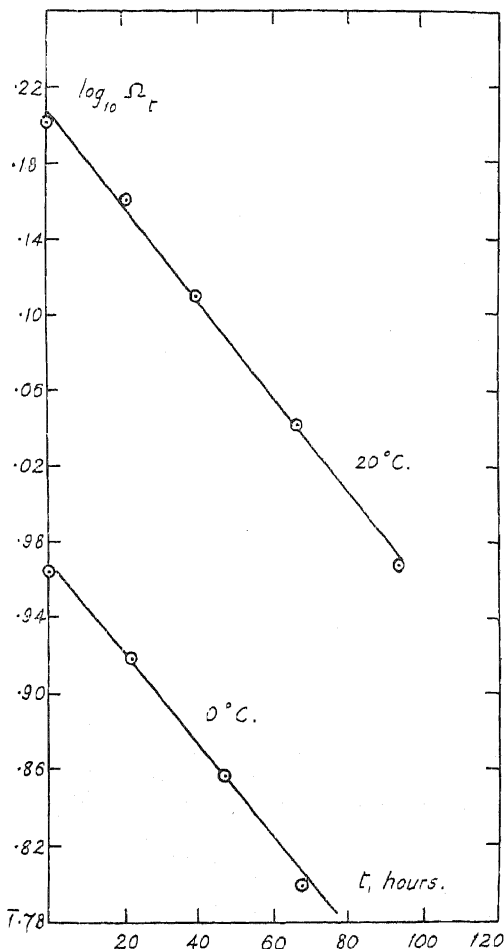


FIG. 2.—Parahydrogen conversion by 0.05 g. Hemin in 10 c.c. N/10 KOH. ( $\Omega$  is the resistance value of the  $pH_2$ , and is proportional to  $C_t$ .)

### Conversion in Solution.

Hemoglobin, hemin and hematin solutions were examined. A sterile solution of blood corpuscles showed no interchange on being shaken for 20 hours with  $D_2$  gas; we can therefore conclude that the dehydrogenases present in blood will not catalyse the interchange between  $D_2$  and water. The *para*  $H_2$  reaction observed was attributed to the hemoglobin, which is the main paramagnetic substance present in the corpuscles. Hemolysis of the corpuscles, by freezing and thawing, produced no appreciable alteration in  $k$ . In the absence of a small

<sup>12</sup> Sachsse, *Z. physikal. Chemie B*, 1934, **24**, 429.

<sup>13</sup> Sachsse, *Z. Electrochemie*, 1934, **40**, 531.



addition of boric acid or thymol, putrefaction set in after 2-3 days' shaking in hydrogen. This was accompanied by a rapid increase in the rate of *para* H<sub>2</sub> conversion, which eventually reached a value 10 to 40 times that for sterile blood. An interchange between D<sub>2</sub> gas and the putrified solution equal in rate to the *para* H<sub>2</sub> conversion was also observed (half-life  $\sim 0.5$  hours for 4 c.c. corpuscles in 10 c.c. solution). This was attributed to the growth of anærobic bacteria, as certain bacterial suspensions are known to catalyse the interchange between D<sub>2</sub> and H<sub>2</sub>O.<sup>14</sup> In Table II we present the data, in the last column giving values of the bimolecular constant

$$K' = \frac{k}{60s} \cdot \frac{(v_g + v_s \cdot s)}{v_s \cdot c},$$

where  $s$  = solubility coefficient of H<sub>2</sub> in the solvent,  $v_g$  = volume of gas phase,  $v_s$  = volume of solution, and  $c$  = concentration of paramagnetic molecule in moles per litre. The application of such a formula to the conversion by ions in water has been demonstrated by Sachsse.<sup>12</sup> For hemoglobin we have taken the molecular weight as 17,000, the Fe-equivalent value (since Fe is assumed to be the paramagnetic centre of the hemoglobin).

TABLE II.—TOTAL REACTION SPACE = 110 C.C., HYDROGEN PRESSURE  $\sim 100$  MM.

Solution.	T° C.	<i>t</i> Hours.	<i>k</i> Hours <sup>-1</sup> .	<i>K'</i> mol. <sup>-1</sup> l. min <sup>-1</sup> .
Hemolysed corpuscles, containing 0.7 g. hemoglobin, in 15 c.c. Ringer solution . . . . .	22	19.7	0.023	49.6
	0	21	0.023	42.5
Above solution converted into hema- tin (0.04 g.) by addition of 15 c.c. 4 N acetic acid . . . . .	22	—	0.0042	4.7
0.05 g. hematin in 10 c.c. N/10 KOH	20	44	0.004	4.4
0.03 g. hematin in 15 c.c. acid EtOH	20	18.5	0.007	2.7
0.05 g. hemin in 10 c.c. N/10 KOH .	20	—	0.0058	6.4
	0	—	0.0055	5.2

Values of  $s$ , H<sub>2</sub>/H<sub>2</sub>O 0° C. = 0.021  
 " " 20° C. = 0.018  
 H<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH 20° C. = 0.086.  
 (Landolt-Bornstein)

Our values of  $k$  for hemin and hematin agree well with those found for O<sub>2</sub> in H<sub>2</sub>O of 10.5,<sup>1</sup> and for Fe<sup>+++</sup> in H<sub>2</sub>O of 7.5.<sup>13</sup> On the simple assumption of identical transition probabilities, this means that there is no appreciable steric factor for the reaction with hematin. Since the porphyrin molecule is approximately flat and contains the active centre, Fe<sup>+++</sup>, in the middle of the structure, we might expect the number of collisions between Fe<sup>+++</sup> and the small H<sub>2</sub> molecule to be not very restricted below the value for the free ion in water. The value of  $k$  for hemoglobin is significantly larger than that for hemin and hematin. Since hemoglobin is pictured as a spherical molecule of molecular weight

<sup>14</sup> Cavanagh, Horiuti and Polanyi, *Nature*, 1934, 133, 797.

64,000, with the four hemes on the surface,<sup>15</sup> the ordinary classical collision number can only be approximately valid. The reaction rate is probably assisted by adsorption of  $H_2$  on the surface of the colloid particle, a rise in reaction probability being occasioned by the time spent in the adsorption layer. For hemin and hemoglobin  $k$  is but little influenced by temperature, but a discussion must await more accurate and extensive measurements. We might expect a rather larger effect than was observed for gaseous  $O_2$  as catalyst, because an activation energy will be required to bring the  $H_2$  into the hydration layer; the results listed are in agreement with this.

The experiments described here were carried out at the University of Manchester, and the author's best thanks are due to Professor M. Polanyi for his interest in them.

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<sup>15</sup> Pauling, *Proc. Nat. Acad. Sci.*, 1935, **21**, 186.

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## LUMINESCENCE OF SUBSTANCES UNDER FLAME EXCITATION.

ADDENDUM TO PAPER PRESENTED TO THE GENERAL DISCUSSION ON  
LUMINESCENCE (SEPTEMBER, 1938).\*

BY L. T. MINCHIN.

*Received 9th November, 1939.*

On page 171 Thomaschek referred to a paper published by Tiede and H. Thomaschek in 1925.<sup>43</sup> This led to the discovery of a group of papers which represent a very important contribution to the work on the subject, and are here summarised. Furthermore, the claim for priority in discovering the phenomenon must now be given either to Donau,<sup>44</sup> who described it seven years before Nichols and Wilbur, or to Balmain, who described it in 1842.<sup>44</sup>

**Conditions of Experiment** (p. 164).—The statement that a hydrogen flame is essential is not in accordance with the experiments of Tiede and Buscher,<sup>41</sup> who found BN excited to luminescence by flames of



and other substances; also by the flame of  $Cl_2$  burning in excess  $H_2$ . If a "flame-separator" is employed, the edge of the inner cone is found somewhat more effective in producing luminescence than the outer mantle of the  $H_2$ -in-air flame.

The luminescence can be observed on a bead in a loop of platinum wire by passing it slowly through the flame. Under these conditions the luminescence of  $CaO$  + trace Bi (cyanide blue colour) and of  $CaO$  + trace Mn (deep yellow) has been observed by the author (L. T. M.).

**Substances showing Luminescence** (p. 165).—To these must be added elements from the odd series of Group 5, Sb, and Bi especially, as activators in  $CaO$ , and also Mn under the same conditions. Boron nitride is also luminescent when crystalline, a condition usually associated with the presence of boric acid. X-ray spectra show that the phenomenon depends on the boron nitride being crystalline.<sup>49</sup> It is also demonstrated

\* *Trans. Faraday Soc.*, 1939, **35**, 163.

that perfectly pure BN is only very faintly flame-luminescent but addition of trace of carbon (1 in 500 to 1 in 10,000) makes it strongly luminescent. It is suggested that C being close in periodic table to B and to N is a suitable atom to form active centres in the lattice of the crystal (*cf.* Cu in ZnS).<sup>43</sup> Zinc sulphide and silicate (Willemite) are strongly luminescent.<sup>41</sup>

**Variation of Luminescence with Temperature** (p. 166).—Paneth and Winternitz<sup>42</sup> suggest that flame performs two functions—to heat and to activate. If specimen has been activated by flame, electrical heating immediately afterwards will produce luminescence. Boron nitride is luminescent up to a bright red heat; when placed in a carbon boat heated electrically to redness, a flame caused it to luminesce blue with much greater intensity. There is, however, no reference to luminescence at higher temperatures than this.

**Quality of Light Emitted** (p. 167).—Tiede and Tomaschek<sup>39</sup> claim to have established the identity of the luminescent radiation emitted by BN under stimulus of flame and of cathode rays. The similarity of the spectral distribution of the light emitted under these stimuli from

CaO + trace Bi, or CaO + trace Mn,

has also been demonstrated.<sup>41</sup> Tiede and Tomaschek in a later paper<sup>43</sup> showed that the effect of varying the proportion of activating C in boron nitride was to alter the intensity of the spectral bands but not their position. Careful comparison is made between these results obtained by excitation with ultra-violet light, cathode rays (in air) and hydrogen flame. In the latter case bands are less well defined and appear to be displaced 5-10  $m\mu$  towards the long-wave end.<sup>43</sup>

**Possible Mechanisms** (p. 167).—Donau suspected an oxidation-reduction process was responsible for the luminescence, but admitted that a specimen of CaO showed no loss in weight on a micro-balance after exposure to flame. The three subsequent papers, however, all reject this explanation, and Paneth suggests bombardment of free ions, or perhaps electrons, from the flame may well be responsible. Tiede and Buscher claimed that ZnS and Willemite would luminesce even when a thin wall of fused silica was interposed between the specimen and the flame. This suggests ultra-violet radiation as the exciting agent, but no definite conclusions are arrived at.

Several workers have also observed<sup>45</sup> that a momentary luminescence is caused by the impingement of a jet of active nitrogen on some substances, and Tiede and Schleede pointed out<sup>46</sup> that the phenomenon resembled flame-excited luminescence. With both forms of excitation some well-known luminescent substances, e.g., Sidot Blende, fail to respond, and in general the effect is most noticeable with compounds of elements of low atomic weight, e.g. LiF, BeCO<sub>3</sub>, BN, Ca(N<sub>3</sub>)<sub>2</sub>. From this analogy it would appear that a further possible explanation of the phenomenon is to be found in the specification of the substances in de-activating the active gas molecules in the flame.

In the light of these papers, it is no longer possible to doubt the reality of this phenomenon, at least as far as the transitory phenomenon at low temperatures is concerned.

Really satisfactory evidence for the existence of a permanent luminescence at temperatures above red heat is still, however, lacking.

<sup>39</sup> Tiede and H. Tomaschek, *Z. Elektrochem.*, 1923, **29**, 303.

<sup>40</sup> Donau, *Monatsheft Chem.*, 1913, **34**, 949; *Wien. Sit.*, 1913, **122**, 335.

<sup>41</sup> Tiede and Buscher, *Ber.*, 1920, **53**, (2), 2206.

<sup>42</sup> Paneth and Winternitz, *Ber.*, 1918, **51**, (2), 1728.

<sup>43</sup> Tiede and H. Tomaschek, *Z. anorg. Chem.*, 1925, **147**, III.

<sup>44</sup> Balmain, *Phil. Mag.*, 1842, **21**, 270 and subsequent papers up to *l.c.* 1846, 25, 87.

<sup>45</sup> Lewis, *Nature*, 1923, **111**, 529. Jevons, *ibid.*, p. 705.

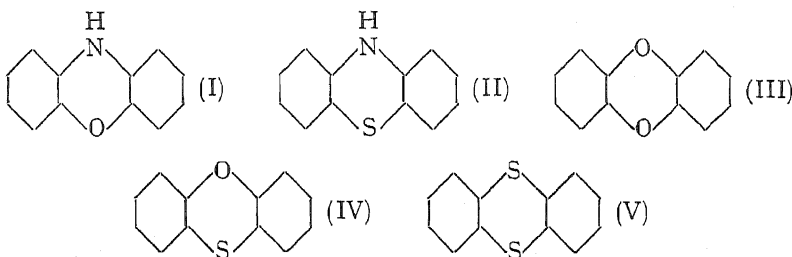
<sup>46</sup> Tiede and Schleede, *Naturwiss.*, 1923, **11**, 765.

# ISOMORPHOUS RELATIONSHIPS OF SOME ORGANIC COMPOUNDS OF ANALOGOUS CONSTITUTION.

By N. M. CULLINANE AND W. T. REES.

Received 4th December, 1939.

In a previous paper<sup>1</sup> the isomorphous relationships of a number of heterocyclic compounds of similar constitution were investigated, the ability of binary mixtures of these substances to yield solid solutions being chosen as the criterion of isomorphism. The work has now been extended, the compounds examined including phenoxazine (I), phenthiazine (thiodiphenylamine) (II), diphenylene dioxide (III), phenoxthionine (IV), and thianthren (V). The results indicate that analogously constituted derivatives of elements of similar type form solid solutions, provided that their spatial structures are also alike.



Simultaneously with this work an X-ray, crystallographic, and optical investigation of these substances is being carried out by Mr. R. G. Wood and his collaborators of the Physics Department of this College, and their results will shortly be published elsewhere.

## Experimental.

### Preparation and Purification of Materials.

**Phenoxazine** was prepared by condensing catechol and *o*-aminophenol in the presence of a little of the aminophenol hydrochloride.<sup>2</sup> Recrystallisation from hot dilute alcohol, followed by sublimation, yielded colourless leaflets, m.p. 156.7°.

The commercial sample of **phenthiazine** was very impure, but when it was boiled for 3 hours with 30 % aqueous sodium hydroxide, washed with water, then sublimed and recrystallised from alcohol, a pure product was obtained, consisting of pale yellow leaflets, m.p. 184.4°. Previous investigators<sup>3</sup> give the m.p. as 180°.

The purification of **diphenylene dioxide** (m.p. 119.9°), **thianthren** (m.p. 156.7°), and **diphenylene oxide** (m.p. 82.4°) have been already described.<sup>4</sup>

<sup>1</sup> Cullinane and Plummer, *J. Chem. Soc.*, 1938, 63.

<sup>2</sup> Kehrman and Neil, *Ber.*, 1914, 47, 3107.

<sup>3</sup> Holzmann, *Ber.*, 1888, 21, 2065; Knoevenagel, *J. prakt. Chem.*, 1914, [ii], 89, 12.

**Phenoxthionine**, prepared by the action of sulphur on diphenyl ether in the presence of anhydrous aluminium chloride,<sup>4</sup> was extracted thoroughly with 30 % aqueous sodium hydroxide solution, washed with water, recrystallised from alcohol, sublimed, and again recrystallised from the same solvent, giving white needles, m.p. 55.7°.

The commercial specimen of **carbazole** was recrystallised from boiling acetone, sublimed, and again recrystallised. Colourless leaflets, m.p. 245.8°, were obtained.

### Results.

Thaw points ( $T_1$ ) and melting temperatures ( $T_2$ ) were determined by the method described in a previous memoir.<sup>1</sup> For the purified compounds  $T_1$  and  $T_2$  did not differ by more than 1°.

A selection of the results is shown graphically in Figs. 1-5, and the complete data are tabulated below.

#### System Phenoxazine-Diphenylene Dioxide (Fig. 1).

Phenoxazine, mols. %	0	9.7	16.5	22.6	29.7	35.2
$T_1$ . . .	119.4°	105.2°	100.4°	96.0°	90.1°	90.3°
$T_2$ . . .	119.9	117.2	114.3	111.8	107.9	93.9
Phenoxazine, mols. %	39.2	51.4	70.9	79.2	87.9	100
$T_1$ . . .	90.2°	89.8°	91.5°	98.2°	114.1°	156.0°
$T_2$ . . .	101.2	123.2	140.1	145.3	150.6	156.7

It is evident from the diagram that a partial series of solid solutions is formed, corresponding to 30 and 70 mols. % of phenoxazine. The eutectic lies at 90°.

#### System Phenthiazine-Phenoxthionine (Fig. 2).

Phenthiazine, mols %	0	11.3	29.2	53.7	66.1	83.2
$T_1$ . . .	55.3°	57.6°	62.3°	70.9°	79.4°	100.3°
$T_2$ . . .	55.7	87.3	123.6	151.8	163.8	175.9
Phenthiazine, mols. %	97.2	100				
$T_1$ . . .	140.2°	183.6°				
$T_2$ . . .	183.3	184.4				

The curve reveals a complete series of solid solutions, the melting-points of all mixtures lying between those of the pure components.

#### System Phenoxazine-Phenthiazine (Fig. 3).

Phenoxazine, mols. %	0	11.8	17.6	36.0	48.3	68.9
$T_1$ . . .	183.6°	148.3°	143.7°	139.8°	140.4°	139.9°
$T_2$ . . .	184.4	178.8	176.3	164.9	156.9	142.6
Phenoxazine, mols. %	73.5	74.4	87.1	94.1	100	
$T_1$ . . .	139.7°	140.0°	139.8°	142.1°	156.0°	
$T_2$ . . .	142.0	143.5	151.1	154.1	156.7	

The system exhibits a eutectic at 140°, with a partial series of solid solutions, of compositions 22 and 93 mols. % of phenoxazine.

#### System Diphenylene Dioxide-Phenoxthionine (Fig. 4).

Phenoxthionine, mols. %	0	5.7	26.1	43.9	66.3	73.0
$T_1$ . . .	119.4°	46.7°	46.8°	46.7°	46.5°	46.5°
$T_2$ . . .	119.9	117.7	106.9	94.4	75.0	62.6
Phenoxthionine, mols. %	78.2	90.4	94.8	100		
$T_1$ . . .	46.4°	46.6°	46.7°	55.3°		
$T_2$ . . .	47.2	52.3	53.9	55.7		

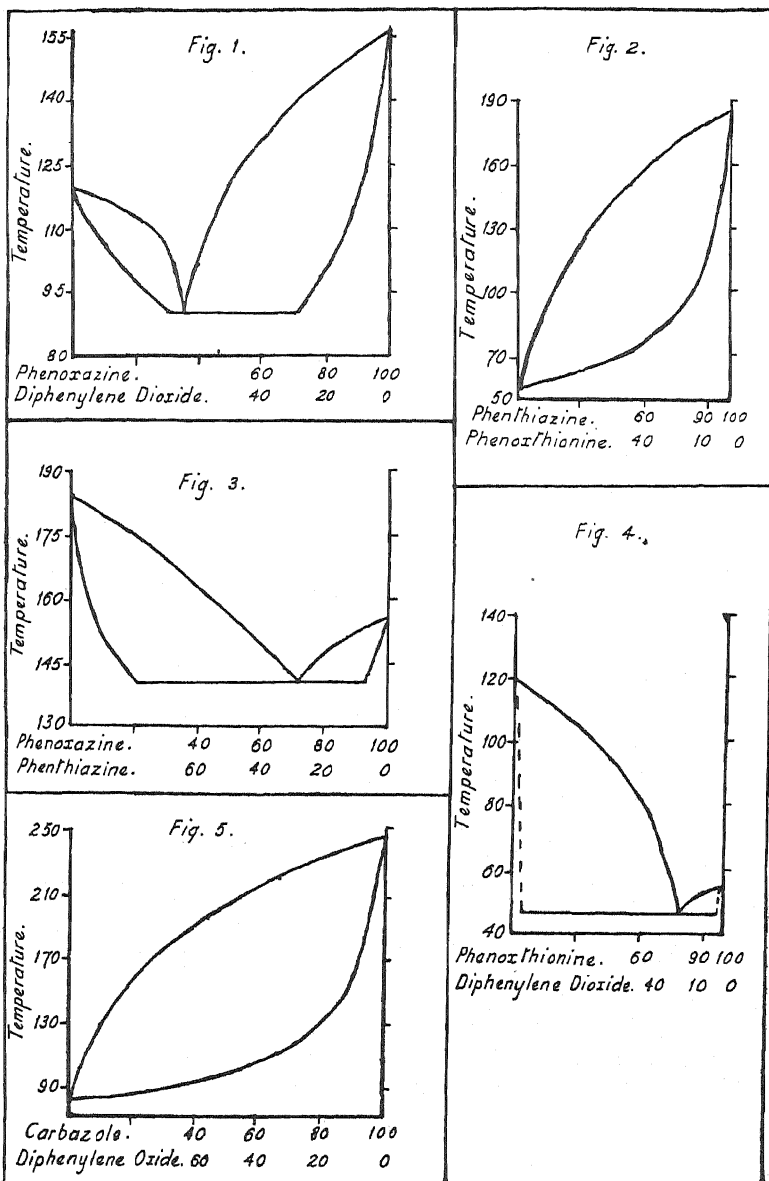
A simple eutectic is shown here, with negligible solid solution formation. The eutectic point is 46.5°, corresponding to 78 mols. % of phenoxthionine.

<sup>4</sup> Suter, McKenzie and Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 718.

## System Phenoxthionine-Thianthren.

Phenoxthionine, mols. %	0	10.0	30.1	48.7	69.2	81.1
$T_1$	155.9°	52.0°	51.9°	51.7°	51.2°	51.6°
$T_2$	156.7	153.6	142.1	126.3	105.5	84.2
Phenoxthionine, mols. %	90.0	93.0	95.4	100		
$T_1$	51.4°	51.9°	51.8°	55.3°		
$T_2$	64.0	52.9	55.1	55.7		

This curve also shows a simple eutectic, at 52°, corresponding to 93 mols. % of phenoxthionine, without any formation of solid solution.



Legends to abscissae give mols. %.

## System Phenoxazine-Phenoxthionine.

Phenoxazine, mols. %	0	2.6	6.7	10.2	16.6
$T_1$ . . .	55.3°	50.3°	50.5°	50.1°	50.1°
$T_2$ . . .	55.7	55.3	54.0	51.2	65.1
Phenoxazine, mols. %	22.9	49.2	78.9	94.3	100
$T_1$ . . .	50.2°	49.9°	50.6°	50.4°	156.0°
$T_2$ . . .	76.6	115.2	142.7	153.8	156.7

The system reveals a simple eutectic, the eutectic temperature being 50°, corresponding to 10 mols. % of phenoxazine.

## System Phenthiazine-Thianthren.

Phenthiazine, mols. %	0	9.4	16.2	26.0	38.2	44.1
$T_1$ . . .	155.9°	141.5°	132.8°	129.4°	130.0°	130.0°
$T_2$ . . .	156.7	153.2	149.5	144.8	135.8	134.4
Phenthiazine, mols. %	56.1	70.9	89.4	95.9	100	
$T_1$ . . .	130.1°	129.5°	131.2°	148.0°	183.6°	
$T_2$ . . .	151.3	164.6	178.5	182.2	184.4	

A partial series of solid solutions is present, corresponding to 20 and 89 mols. % of phenthiazine. The eutectic temperature is 130°.

## System Phenoxazine-Thianthren.

Thianthren, mols. %	0	3.3	24.1	43.9	45.8	53.1
$T_1$ . . .	156.0°	118.0°	117.6°	117.5°	117.7°	117.5°
$T_2$ . . .	156.7	154.9	139.0	120.2	118.8	126.2
Thianthren, mols. %	74.9	94.6	100			
$T_1$ . . .	117.7°	117.8°	155.9°			
$T_2$ . . .	143.2	154.3	156.7			

The system phenoxazine-thianthren shows a simple eutectic, with no observable solid solution formation. The eutectic point is 118°, corresponding to 45 mols. % of thianthren.

## System Phenthiazine-Diphenylene Dioxide.

Diphenylene Dioxide, mols. %	0	5.0	21.1	48.5	78.0
$T_1$ . . .	183.6°	108.1°	108.3°	108.4°	108.3°
$T_2$ . . .	184.4	182.8	174.2	151.8	116.6
Diphenylene Dioxide, mols. %	83.2	89.2	98.1	100	
$T_1$ . . .	108.5°	108.6°	108.7°	119.4°	
$T_2$ . . .	110.0	114.3	119.6	119.9	

The system forms a simple eutectic, with negligible solid solution formation. The eutectic lies at 108.5°, and corresponds to 16 mols. % of thianthren.

## System Carbazole-Diphenylene Oxide (Fig. 5).

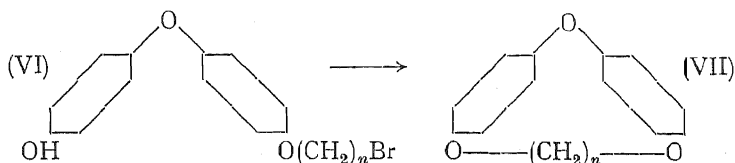
Carbazole, mols. %	0	10.2	24.7	43.8	66.9	85.9	100
$T_1$ . . .	81.5°	83.5°	87.5°	95.4°	109.5°	141.2°	245.1°
$T_2$ . . .	82.4	128.4	166.0	196.3	219.6	236.8	245.8

An uninterrupted series of solid solutions is revealed, the melting-points of all mixtures lying between those of the pure components.

### Discussion of Results.

Recent investigations suggest that the phenomenon of isomorphism is connected with similarity in molecular configuration rather than chemical constitution. Thus in the view of Niggli<sup>5</sup> the ability to form solid solutions is due to similarity rather of geometrical form than of chemical behaviour. He points out that only in so far as atoms are sufficiently closely related chemically to yield geometrically similar types of compounds will isomorphism be predominantly connected with groups of related elements in the Periodic System. Moreover Pirsch<sup>6</sup> states that the real criterion of the isomorphous miscibility of compounds is similarity in the shape of the space occupied by the molecules. He concludes, and supports his conclusions by means of a number of examples, that if compounds, though differing in chemical constitution, approach each other in spatial configuration, mixed crystals will be formed. The results obtained in the present work are of interest in this connection.

From considerations of electric dipole moment,<sup>7</sup> and the yields obtained in the formation of cyclic ethers by ring closure of the type<sup>8</sup> (VI)  $\rightarrow$  (VII)



it is concluded that the valency angle of oxygen in diphenyl ether has a value somewhat greater than  $120^\circ$ , while a value of  $118 \pm 3^\circ$  for the oxygen angle in *p*:*p'*-diiododiphenyl ether was obtained by Maxwell, Hendricks and Mosley<sup>9</sup> from electron diffraction measurements. In dimethyl ether, on the other hand, the oxygen valency angle approximates to the tetrahedral value of  $109^\circ 28'$ .<sup>10</sup> The enlargement of the angle in the case of diphenyl ether may be due to mutual repulsion between the phenyl groups, as suggested by Stuart,<sup>11</sup> or to resonance between the normal molecule and the two possible excited states, as envisaged by Sutton and Hampson.<sup>12</sup>

Turning now to the case of diphenyl sulphide, we find from the dipole moment measurements of Sutton and Hampson,<sup>12</sup> and the X-ray experiments of Kohlhaas,<sup>13</sup> confirmed by the yields obtained in the formation of cyclic ethers of the type mentioned above (with sulphur as the central atom),<sup>8</sup> that the sulphur valency angle in diphenyl sulphide is in the neighbourhood of  $112^\circ$ . This appears to be larger than the

<sup>5</sup> Niggli, *Z. Krist.*, 1921, **56**, 167; cf. Ferrari and Baroni, *Atti. Accad. Lincei* 1928, [vi], **7**, 848.

<sup>6</sup> Pirsch, *Ber.*, 1936, **69**, 1323.

<sup>7</sup> Coop and Sutton, *J. Chem. Soc.*, 1938, 1869.

<sup>8</sup> Lüttringhaus, *Ber.*, 1939, **72**, [B], 887, 907.

<sup>9</sup> Maxwell, Hendricks and Mosley, *J. Chem. Physics*, 1935, **3**, 699.

<sup>10</sup> Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 477.

<sup>11</sup> Stuart, *Z. physikal. Chem.*, 1937, **B**, **36**, 155.

<sup>12</sup> Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 953.

<sup>13</sup> Kohlhaas and Lüttringhaus, *Ber.*, 1939, **72**, [B], 897.



corresponding angle in hydrogen sulphide<sup>14</sup> or dimethyl sulphide,<sup>15</sup> and can be accounted for in the same way as in the case of diphenyl ether.

Apropos of this stereo-chemical dissimilarity between diphenyl ether and sulphide, the fact that these substances form only a limited series of solid solutions may be noted. Furthermore, according to Thompson and Turner,<sup>16</sup> the preferred valency angle of selenium is very close to that of sulphur, and Pascal<sup>17</sup> has shown that diphenyl sulphide and selenide give a continuous series of solid solutions (type III, Roozeboom).<sup>18</sup>

In diphenylene oxide and sulphide the heterocyclic atoms form part of a rigid system, and a closer similarity in the valency angles than in the corresponding diphenyl derivatives is probably enforced. The system diphenylene oxide-sulphide thus exhibits a complete series of mixed crystals<sup>1</sup> (type III, Roozeboom).<sup>18</sup>

Diphenylene dioxide possesses a planar molecule, as evidenced by the fact that it has zero dipole moment.<sup>19</sup> This is confirmed by the experiments of Wood, which show that the molecule probably has a centre of symmetry, which would be impossible if it were folded. The corresponding sulphur compound thianthren, on the other hand, with a large moment, is folded along the S—S axis.<sup>20</sup> In this connection it may be noted that Cullinane and Plummer<sup>1</sup> found that the system diphenylene dioxide-disulphide formed a eutectic with negligible solid-solution formation, while thianthren and selenanthren, which are considered to be folded to a similar extent,<sup>16</sup> gave an uninterrupted series of mixed crystals (type I, Roozeboom).<sup>18</sup>

If we now consider phenoxthionine, and assume that in all possible configurations the centres of the oxygen and sulphur angles remain in the plane of the two benzene rings, and that the O—C and S—C bonds make angles of 120° with the adjacent bonds of the aromatic nucleus,<sup>18</sup> taking the radii of aromatic carbon, oxygen, and sulphur to be 0.7, 0.66, and 1.05 Å. respectively, we obtain the following relationships between the oxygen angle, the sulphur angle, and the angle of fold about the O—S axis:

O angle . . . . .	100°	110°	120°	130°	133°
S angle . . . . .	84°	92°	99°	105°	107°
Angle of fold . . . .	113°	127°	142°	162°	180°

As it is unlikely that oxygen would tolerate a greater angle than 130°, we conclude that the molecule is folded.

The results obtained in the present work show that the planar diphenylene dioxide forms a eutectic with phenoxthionine (Fig. 4) without any appearance of mixed crystal formation. Moreover, Wood's experiments show that there is a pronounced dissimilarity in the structures of the two substances.

Not much is known concerning the preferred valency angle of

<sup>14</sup> Cross, *Physical Rev.*, 1935, 47, 7; Dadieu and Kohlrausch, *Physikal. Z.*, 1932, 33, 165.

<sup>15</sup> Pai, *Ind. J. Physics*, 1934, 9, 121; Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, 58, 2040.

<sup>16</sup> Thompson and Turner, *J. Chem. Soc.*, 1938, 30.

<sup>17</sup> Pascal, *Bull. Soc. chim.*, 1912, 11, 30.

<sup>18</sup> Roozeboom, *Z. physikal. Chem.*, 1899, 30, 385.

<sup>19</sup> Bennett, Earp and Glasstone, *J. Chem. Soc.*, 1934, 1180.

<sup>20</sup> Bennett and Glasstone, *J. Chem. Soc.*, 1934, 128; cf. Bergmann, *Ber.*, 1932, 65, 457.

nitrogen, although in ammonia<sup>21</sup> and trimethylamine<sup>22</sup> it appears to approximate to the tetrahedral value. In diphenylamine the same type of resonance can occur as in diphenyl ether, and this would cause an enlargement of the nitrogen angle, though to what extent is not known. In 9:10-dihydrophenazine and its derivatives, where resonance can also occur, Sutton and Hampson<sup>12</sup> suggest that the molecule is planar as in diphenylene dioxide. On the other hand Campbell, Le Fèvre, Le Fèvre and Turner<sup>23</sup> are of opinion that 9:10-dihydro- and 9:10-dimethyl dihydro-phenazine, which appear to have definite though small dipole moments, are folded.

Phenazine itself, however, which possesses zero dipole moment, is undoubtedly flat,<sup>23</sup> as would be expected from the widening of the nitrogen angle due to the presence of the double bond, a conclusion confirmed by Wood.

Making the same assumptions in the case of phenthiazine as for phenoxthionine, and taking the radius of the nitrogen atom as 0.7 Å., we obtain the following relationships between the nitrogen angle, the sulphur angle, and the angle of fold about the N—S axis:

N angle	.	.	.	100°	110°	120°	130°	132°
S angle	.	.	.	85°	93°	100°	107°	108°
Angle of fold	.	.	.	114°	128°	143°	166°	180°

As a valency angle greater than 130° is scarcely likely for nitrogen, a folded molecule seems to be the most plausible structure for phenthiazine. A nonplanar molecule is shown to be compatible with Wood's results, though definite proof of such a configuration has not been obtained. In the present work, the temperature-concentration diagram (Fig. 2) shows that the system phenthiazine-phenoxthionine exhibits an unbroken series of mixed crystals (type I, Roozeboom).<sup>18</sup> Moreover, the system diphenylene dioxide-phenthiazine forms a eutectic, no solid solution being present.

In the case of phenoxazine, we obtain the following relationships between the nitrogen angle, the oxygen angle, and the angle of fold about the N—O axis:

N angle	.	.	.	.	.	100°	110°	119°
O angle	.	.	.	.	.	102°	112°	121°
Angle of fold	.	.	.	.	.	126°	145°	180°

The above results suggests that there is only slight, if any, folding of the molecule. The systems diphenylene dioxide-phenoxazine (Fig. 1) and phenthiazine-phenoxazine (Fig. 3) both reveal a limited series of solid solutions (type V, Roozeboom).<sup>18</sup>

Referring now to the corresponding carbon compounds, in methane the carbon valency angle has the tetrahedral value of 109° 28'. Furthermore Lüttringhaus<sup>8</sup> concludes from his ring closure experiments that the central carbon angle in diphenyl methane is  $110 \pm 3^\circ$ , so that there is no appreciable enlargement. The fact that no resonance effect is possible in this compound, such as that proposed, for example, in the case of diphenyl ether, would account for the absence of any pronounced

<sup>21</sup> Dennison and Uhlenbeck, *Physical Rev.*, 1932, 41, 313; Lueg and Hedfeld, *Z. Physik*, 1932, 75, 599.

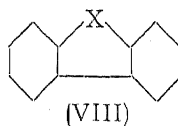
<sup>22</sup> Brockway and Jenkins, *loc. cit.*<sup>15</sup>

<sup>23</sup> Campbell, Le Fèvre, Le Fèvre and Turner, *J. Chem. Soc.*, 1938, 407; cf. Bergmann, Engel and Meyer, *Ber.*, 1932, 65, 446.

alteration in the angle. In this connection the fact that diphenyl methane and diphenyl ether form a eutectic, without any mixed crystals being formed, is noteworthy.<sup>24</sup>

Now 9 : 10-dihydroanthracene appears to have a measureable dipole moment,<sup>25</sup> indicating that its molecule is folded about the  $\text{CH}_2\text{--CH}_2$  axis, as is to be expected if the carbon valency angles are less than  $120^\circ$ . On the other hand, anthracene possess a planar structure,<sup>25</sup> and this can be explained by the carbon angles of the centre ring being increased owing to the double bonds attached to them. Moreover, anthracene and its dihydro-derivative give a eutectic, no solid solution being observed.<sup>26</sup>

As already mentioned, compounds of the type (VIII) possess a fairly rigid structure, and though X may vary, a similar valency angle is probably enforced. Thus the systems fluorene-diphenylene oxide,<sup>24</sup> carbazole-diphenylene oxide, diphenylene oxide-diphenylene sulphide,<sup>1</sup> and diphenylene sulphide-diphenylene selenide<sup>1</sup> all yield continuous series of solid solutions.



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<sup>24</sup> Lüttringhaus, *Annalen*, 1937, 528, 229.

<sup>25</sup> Robertson, *Proc. Roy. Soc.*, 1933, 140, 79.

<sup>26</sup> Grimm, Günther and Tittus, *Z. physikal. Chem.*, 1931, B, 14, 210.

## REVIEWS OF BOOKS.

**Der Disperse Bau der Festen Systeme.** By DR. D. BALAREW.  
(Dresden and Leipzig : Theodor Steinkopf. Pp. vi + 240, with 45 illustrations. Price, R.M. 7.50 : bound, R.M. 8.62.)

This book sets out to discuss the nature of "impurity" in the solid state, and therefore deals in considerable detail with the properties of the "real" and the "ideal" crystal. Borderland phrases like amorphous bodies and super-cooled liquids receive attention in much the same way. There is also an interesting section upon velocity of crystallisation, both spontaneous and linear. The former is of dimensions Number of grains/Time, whereas the latter is Length/Time, and thus more truly a velocity in the normal sense.

A good feature is the resumé at the end of each chapter, which helps to balance to some extent the tendency to "write round the references." But the specialist will welcome Professor Balarew's work for reference purposes, and for its thoroughness.

F. I. G. R.

## STUDIES IN MEMBRANE PERMEABILITY. II. THE ADSORPTION OF SUCROSE AND TWO SALTS ON CUPRIC FERROCYANIDE.

BY B. C. McMAHON, E. J. HARTUNG AND W. J. WALBRAN.

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The adsorption of solutes by cupric ferrocyanide is of interest in regard to the composition of the precipitated material and to its properties as an osmotic membrane, but relatively little work with any claim to accuracy has been devoted to the question. The investigations of Tinker in 1916<sup>1</sup> merely showed that dried cupric ferrocyanide removed water preferentially to sugar from an aqueous sucrose solution. One of the present authors in 1919<sup>2</sup> gave careful measurements on the adsorption of KCl and K<sub>2</sub>SO<sub>4</sub> from aqueous solution by the precipitated gel which showed that K<sub>2</sub>SO<sub>4</sub> was definitely adsorbed to a greater extent than KCl, and this result was correlated with the greater diffusibility of the chloride through the cupric ferrocyanide membrane. These otherwise very consistent measurements are unreliable at low concentrations, owing to the presence of residual salt in the washed gel. H. B. Weiser in 1930<sup>3</sup> published analyses of solutions in which cupric ferrocyanide had been precipitated from aqueous CuCl<sub>2</sub> by K<sub>4</sub>Fe(CN)<sub>6</sub>, Na<sub>4</sub>Fe(CN)<sub>6</sub>, and H<sub>4</sub>Fe(CN)<sub>6</sub> from which the extent of adsorption of the precipitant was inferred. As a typical case, free K<sub>4</sub>Fe(CN)<sub>6</sub> did not appear in solution until the molar ratio of excess K<sub>4</sub>Fe(CN)<sub>6</sub> to Cu<sub>2</sub>Fe(CN)<sub>6</sub> in the precipitate was about 0.4, which Weiser regarded as irreversible adsorption of the precipitant on pure Cu<sub>2</sub>Fe(CN)<sub>6</sub>, while subsequent molar ratios up to 0.8 in solutions containing excess soluble K<sub>4</sub>Fe(CN)<sub>6</sub> were classed as due to reversible adsorption. These ratios were lower for Na<sub>4</sub>Fe(CN)<sub>6</sub> and for H<sub>4</sub>Fe(CN)<sub>6</sub> but were still large. Experiments with K<sub>2</sub>SO<sub>4</sub> and CuCl<sub>2</sub> on material precipitated by H<sub>4</sub>Fe(CN)<sub>6</sub> indicated small positive adsorptions in each case. A similar point of view is shown in a later paper<sup>4</sup> using cupric ferricyanide as an adsorbent.

It is, however, unusual to class composition changes of such magnitude, other than those due to hydration of gels, as demonstrating adsorption. Much work has been done on the composition of precipitated cupric and other ferrocyanides<sup>5</sup> from which it seems clear that these substances form solid solutions very readily with soluble ferrocyanides, and the composition of these solid solutions varies, as one would expect, with the composition of the liquid phase from which they separate. Moreover, the work of Messner<sup>6</sup> and of Reihlen and Zimmermann<sup>7</sup> makes it clear that part of the copper in Cu<sub>2</sub>Fe(CN)<sub>6</sub> is in the anionic

<sup>1</sup> F. Tinker, *Proc. Roy. Soc., A*, 1916, **92**, 357; 1917, **93**, 266.

<sup>2</sup> E. J. Hartung, *Trans. Faraday Soc.*, 1920, **15**, 150.

<sup>3</sup> H. B. Weiser, *Coll. Symp. Ann.*, **7**, 275; *J. phys. Chem.*, 1930, **34**, 335.

<sup>4</sup> H. B. Weiser, *ibid.*, 1826.

<sup>5</sup> E. Müller, Wegelin and Kellerhoff, *J. prakt. Ch.*, 1912, (2), 86, 82.

<sup>6</sup> Messner, *Z. anorg. Chem.*, 1895, **8**, 368; **9**, 126.

<sup>7</sup> H. Reihlen and W. Zimmermann, *Annalen*, 1927, **451**, 75.

form, so that the salt should be formulated  $\text{Cu}[\text{CuFe}(\text{CN})_6]$ . This is borne out by the X-ray analysis of Keggin and Miles<sup>8</sup> which indicates that the structure is probably akin to Prussian blue, with alternate bivalent copper and iron atoms occupying the corners of a cubic lattice and cyanogen groups along the edges. The position of the bivalent copper cations is doubtful. One might suppose them to occupy the centres of alternate cubical cells, but Fordham and Tyson,<sup>9</sup> whose electron diffraction studies confirm completely the cubical lattice with 5 Å. spacing, were not able to find them at all. They believe, however, that they cannot lie in these positions without giving rise to diffractions of an intensity too great to be overlooked. Nevertheless, these cations must be somewhere in the lattice, and it is possible that they may be distributed statistically to give a pseudo-cubic symmetry, in conformity with other known cases. Definite crystalline compounds of the type  $\text{M}^{++}[\text{CuFe}(\text{CN})_6]$  are known in which M is an alkaline earth metal and where one may reasonably assume complete replacement of cationic copper. Complete replacement by Na or K would involve filling the centres of all cells as in the Prussian blues, and this appears also here to have been attained.<sup>6</sup> One may therefore regard precipitated cupric ferrocyanide as exhibiting partial replacement of this kind, and not adsorption of one ferrocyanide in very large amount on another. The X-ray evidence adduced by Weiser, Milligan and Bates<sup>10</sup> in support of adsorption does not conflict with the view given above. These authors assume that either adsorption or double-salt formation takes place; they do not consider the possibility of solid solution, and rule out double-salt formation on the ground that their X-ray photographs show no special structure to be developed in gels containing much alkali ferrocyanide. But their diffraction patterns of gels precipitated by  $\text{K}_4\text{Fe}(\text{CN})_6$  at different excess concentrations, and by  $\text{H}_4\text{Fe}(\text{CN})_6$ , are identical, thus showing that their method is unable to distinguish between cationic copper, potassium and hydrogen.

Precipitation of cupric ferrocyanide in the continuous presence of excess cupric ions excludes adsorption of ferrocyanide ions, yet the gel so prepared may contain much firmly bound alkali ferrocyanide. On washing it peptises ultimately due to cationic loss to the solution, forming the usual negative sol; this is promoted by addition of soluble ferrocyanide, due to true adsorption. We have found that the gel prepared from excess  $\text{CuAc}_2$  and the acid itself cannot be peptised by washing, although it contains some excess of ferrocyanic acid over the stoichiometric ratio, yet a slight concentration of the acid or a soluble ferrocyanide peptises the washed gel at once as the anions are adsorbed. It is evident therefore that soluble ferrocyanides are unsuitable solutes for adsorption work with cupric ferrocyanide because of their solid-solution forming propensity. The present work was undertaken to afford accurate data for sucrose and two salts for which reliable diffusion data through a cupric ferro-cyanide membrane are also available.<sup>11</sup> Great pains were taken in regard to analytical procedure and purity of reagents, and distilled water was prepared in silica.

<sup>8</sup> J. F. Keggin and F. D. Miles, *Nature*, 1936, **137**, 577.

<sup>9</sup> S. Fordham and J. T. Tyson, *J. Chem. Soc.*, 1937, 483.

<sup>10</sup> H. B. Weiser, W. O. Milligan and J. B. Bates, *J. phys. Chem.*, 1938, **42**, 945.

<sup>11</sup> E. J. Hartung, F. H. Kelly and J. Wertheim, *Trans. Faraday Soc.*, 1937, **33**, 398.

### Experimental.

Cupric ferrocyanide was prepared by precipitating excess of  $\text{CuAc}_2$  solution with aqueous  $\text{H}_4\text{Fe}(\text{CN})_6$ , the acid being made by the method of Cumming.<sup>12</sup> As the gel so made could not be peptised by washing, all soluble matter was conveniently removed from it by centrifuging. This behaviour rendered subsequent separation from sucrose solutions relatively easy, whereas the gel prepared from alkali ferrocyanide peptises before soluble electrolytes are completely removed and then cannot be separated from sucrose solutions without altering the composition of the latter. After much preliminary work we selected the gel made from ferrocyanic acid and at least 10 % excess of copper acetate, and have used it exclusively. It was stored in distilled water at room temperature and appears then to keep indefinitely. After vigorous shaking, the turbid suspension could be sampled with a wide-mouthed pipette with less than 0.1 % variation. Analysis proved difficult, the method adopted finally being to determine the Cu/Fe ratio gravimetrically. Different batches of gel agreed closely in giving this ratio as 2.20 ( $\text{Cu}_2\text{Fe}(\text{CN})_6$  requires 2.28) indicating that the material contained 3.6 moles  $\text{H}_4\text{Fe}(\text{CN})_6$  per 100 moles of  $\text{Cu}_2\text{Fe}(\text{CN})_6$ . For comparison, the gel made from alkali ferrocyanide and 25 % excess copper salt gave after complete washing a Cu/Fe ratio of 2.06, indicating 10.4 moles of  $\text{K}_4\text{Fe}(\text{CN})_6$  per 100 moles of  $\text{Cu}_2\text{Fe}(\text{CN})_6$ .

### Adsorption of Sucrose.

Measurements were performed in the usual way in stoppered capped 100 c.c. glass tubes rotated for two days (an ample time) in a thermostat at 25°. After centrifuging, the clear liquid was in part removed and the pipette washed back into the tube. The sucrose was determined with the Zeiss interferometer, and then more sucrose and water added to the tube for a new experiment, the synthetic composition of the tube contents being controlled entirely by weight. Ascending and descending concentration series were performed on the same tubes, and each experimental point was determined in quadruplicate with four different tubes and often different batches of gel. This method of working is convenient, but may introduce cumulative errors. However, the ascending and descending series agreed very well, particularly at the lower concentrations, thus indicating the practical reversibility of the phenomena and the dependability of the experimental results. The ratio of gel (estimated as dry material) to water was always maintained constant at 4.6 %; it is difficult to work with higher ratios than this owing to the pasty nature of the systems.

### Adsorption of $\text{NaCl}$ and $\text{Na}_2\text{SO}_4$ .

The general procedure for each salt followed closely that for sucrose, and the same gel-water ratio was always maintained. In spite of all care, however, the results are definitely less concordant. Moreover, a slight amount of cationic displacement of Cu from the gel by Na was observed, the maximum concentration of  $\text{Cu}^{++}$  ever appearing in solution being about 40 mg. per litre but usually very much less was present. As appreciable errors might have been introduced, the Cu was determined in the withdrawn sample colorimetrically, and a compensating amount added to the tube for the next determination to avoid cumulative loss of Cu, the interferometer readings being also corrected. Numerous experiments with variation of procedure indicated that only a very small amount of copper may be displaced in this way, and that the exchange takes place largely at the start of a series of measurements with the same material. Individual

<sup>12</sup> Cumming, *J. Soc. Chem. Ind.*, 47, 84.

experiments on tubes of fresh gel instead of series with the same tubes were performed, but this method, besides being very wasteful of time and material, afforded no greater concordance in results. It is possible that cationic exchange may affect the adsorptive powers of the gel for anions but prolonged investigation has failed to afford any positive evidence for this. This applies also to those cases where a second form of cupric ferrocyanide appeared in some of the tubes (as described later). Very early changes in adsorptive power may take place after addition of salt to the gel, but we have not been able to devise any method for proving this with cupric ferrocyanide systems where adsorption equilibrium is rapidly attained. In no case was anionic exchange noted.

### Adsorption of NaCl and Na<sub>2</sub>SO<sub>4</sub> in Presence of Sucrose.

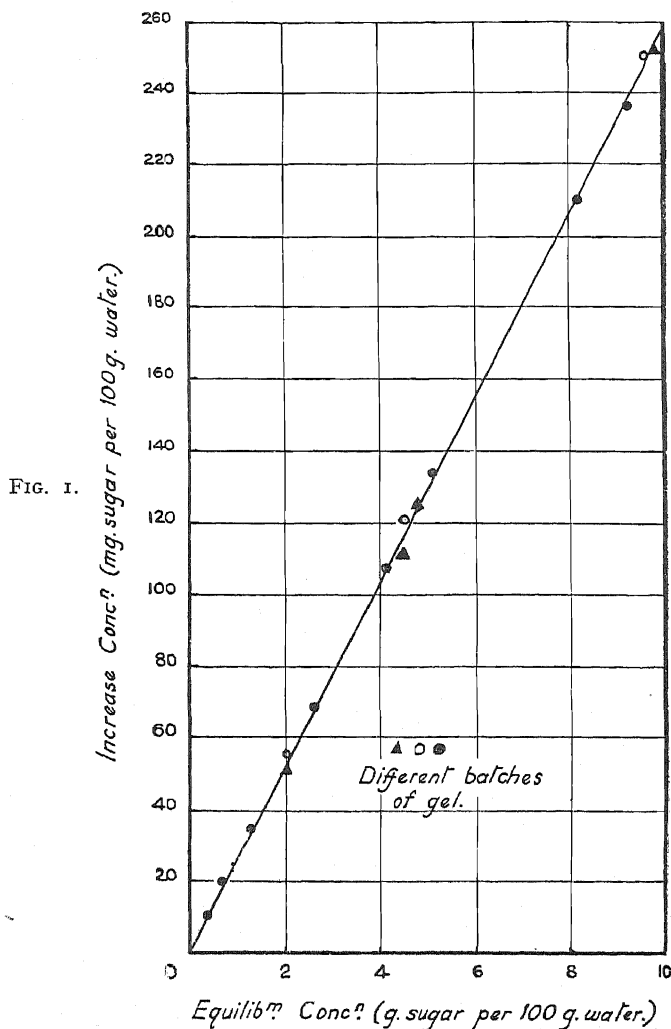
These experiments were undertaken in the hope of using sucrose as a reference substance to determine the hydration of the gel. A special form of weight pipette enabled samples to be taken from the tubes so that the total sample could be accurately weighed. Chloride was estimated volumetrically and sulphate gravimetrically after due investigation of the errors involved. Sucrose was determined with the interferometer by matching in each case with comparison solutions in which the concentrations of the other solutes were maintained at the predetermined analytical values. The sucrose-water ratio was always 5 %.

### Discussion of Results.

The results of the experiments with sucrose alone are shown in Fig. 1, where increase in concentration of the solution over the synthetic sugar—total water ratio (in mg. per 100 g. water) is plotted against the equilibrium concentration of sucrose (in g. per 100 g. water). Each point on the graph represents the mean of 4 determinations on different tubes, which were usually so closely concordant that they could not be shown apart on the scale of the curve, and three different batches of gel are represented. It will be seen that adsorption is always negative, that the curve shows excellent linearity and passes through the origin. Without making artificial and unlikely assumptions as to the way in which sucrose adsorption may vary with concentration, the only interpretation of these results is that the bound water of the gel (*i.e.*, water unavailable to sucrose) is constant and that there is no sucrose adsorption at all. It is at first sight remarkable that the bound water should not vary with sucrose concentration, *i.e.*, with change in the activity of the water in solution. So far as we are aware, such behaviour is quite exceptional (see the review by Briggs<sup>13</sup>). The difficulty is removed if we consider the bound water to consist of two parts—a small amount of truly adsorbed or polarised water on the surface or even in the structure of the gel crystallites, and a larger amount of imbibed water between them. If all of this bound water is out of reach of the sucrose, which is likely since even very thin membranes of cupric ferrocyanide are impermeable to sucrose, calculation from the curve shows that 10.6 moles of water are bound by one mole of Cu<sub>2</sub>Fe(CN)<sub>6</sub>. Such a degree of hydration is more characteristic of hydrophilic than of electrostatic sols of this type. Moreover, it is impossible to find room for such a large amount of water in the Cu<sub>2</sub>Fe(CN)<sub>6</sub> lattice, or even on its surface by polarised adsorption, and it is likely that most of it is merely imbibed by the gel, being thereby excluded from the large sugar molecules in the same way that water in

<sup>13</sup> D. R. Briggs, *J. phys. Chem.*, 1932, 36, 367.

swollen gelatine may be excluded to colloidal particles of suitable size. It is then understandable that the polarised water in the gel may vary with sucrose concentration as one would expect, although the total polarised and imbibed water remains independent of it because this bound water is in effect determined in the gel by spatial considerations.



If this argument be correct however, sucrose cannot be used with security to measure the amount of bound water in the gel in relation to other solutes. For if these solutes are able to penetrate the cupric ferrocyanide membrane, it is likely that the imbibed water may be available to them although not to sucrose. Indeed the results for NaCl and  $\text{Na}_2\text{SO}_4$  with and without sucrose in solution give some indication that this is the case.

In Figs. 2 and 3 respectively are plotted for NaCl and  $\text{Na}_2\text{SO}_4$  increase in concentration of the solution over the synthetic concentration (in



mg. ions per 100 g. water) with and without sucrose present in fixed concentration of 5 g. per 100 g. water against the equilibrium concentra-

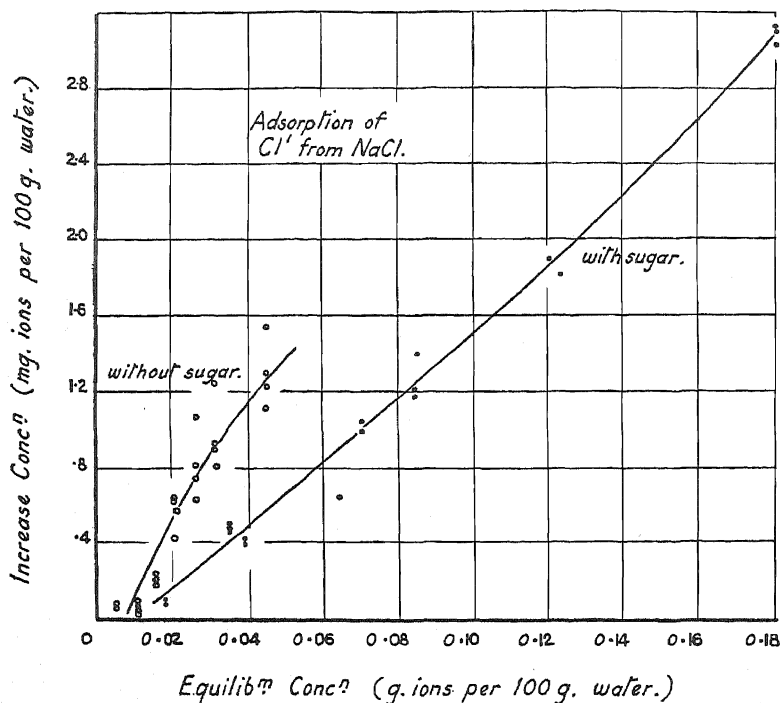


FIG. 2.

tion of the solution (in g. ions per 100 g. water). In spite of all care in the analytical work, considerable deviations in the experimental points are

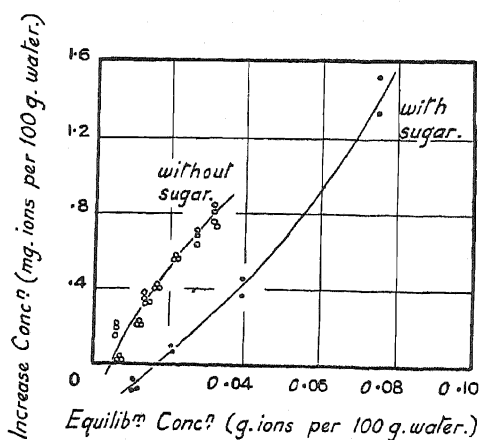


FIG. 3.

shown since the errors are thrown on small differences. There is, however, no doubt about the directions of the curves in each case. The apparent anionic adsorption is negative, but there is evidence that it becomes definitely positive at low concentrations, especially for sulphate, as the curves do not pass directly through the origin. It is also evident that the presence of sucrose diminishes the negative anionic adsorption in each case, but it is possible to account for this by supposing that sucrose diminishes the polarised water on the gel owing to the lowered activity of the water in the solution while the imbibed water is available to the ions

of the salts, which one would expect owing to their ready penetration of the gel membrane.

The negative adsorption of NaCl and  $\text{Na}_2\text{SO}_4$  is in marked contrast with the results obtained by one of us<sup>2</sup> for KCl and  $\text{K}_2\text{SO}_4$  on the gel prepared from  $\text{K}_4\text{Fe}(\text{CN})_6$  which showed pronounced positive adsorption. No significant differences in adsorption between NaCl and  $\text{Na}_2\text{SO}_4$  have been found, in spite of the greater diffusibility of NaCl through the cupric ferrocyanide membrane, in one case in the ratio of 4.5 to 1.<sup>11</sup> Our results show therefore no connection in the case of these salts between adsorption and diffusibility through the membrane, although they indicate that the indiffusible non-electrolyte sucrose is not adsorbed at all. The results of Collander<sup>14</sup> with cupric ferrocyanide and of Michaelis<sup>15</sup> and co-workers with celloidin indicate that these membranes behave like molecular sieves to diffusing non-electrolytes, so that molecular diameter in relation to pore size is the dominating factor. The problem is less simple in the case of electrolytes, where differential permeability to ions is related to differential adsorption. Work now in progress in this laboratory on cupric ferrocyanide membrane potentials in presence of salts confirms substantially this view developed by Michaelis,<sup>16</sup> in spite of our difficulty in establishing differences in adsorption experimentally with NaCl and  $\text{Na}_2\text{SO}_4$  where they might be expected on other grounds.

### Two Forms of Hydrated Cupric Ferrocyanide.

As some of the experiments with the salt solutions in contact with the gel progressed, it was noted that the gel showed a tendency to separate on centrifuging into two layers which in certain cases were very distinct and striking. The upper layer was light reddish-brown and the lower the original deep chocolate. The pale form appeared to be more finely divided than the other; it was more easily dispersed on shaking and peptised readily on washing but did not change colour again on coagulation with  $\text{CuSO}_4$ . Separation of the two layers for analysis was fairly easily accomplished and the Cu/Fe ratio was determined for each. The average value for the pale material was 2.18 and for the dark 2.17 while that of the original was 2.20 to 2.21. Both show therefore loss of Cu which, as before stated, was found in solution but the analytical differences are trifling in view of the great alteration in appearance. We were also unable to detect any certain differences in adsorptive power between the two forms and have not yet succeeded in discovering their nature. Ionic exchange cannot be responsible for the formation of the pale variety for we have sometimes found it in sucrose solutions in the absence of electrolytes. Little difference in hydration of the two forms can be detected; both become lighter in colour on drying, the pale form being then yellow, but the original appearance returns in each case on hydration in moist air and the differences in colour persist.

If the dry yellow form be exposed to benzene or ether vapour, or wetted with the liquids, it rapidly becomes deep indigo, the colour being roughly complementary to that of the dry material. This change is reversible and can be induced repeatedly. Preliminary experiments give some indication that the indigo material is a new phase, as judged from benzene vapour pressure measurements in contact with it, and the matter is now being further investigated.

<sup>14</sup> R. Collander, *Kolloidchem. Beihefte*, 1924, **19**, 72.

<sup>15</sup> L. Michaelis, *Coll. Sym. Monog.*, 1928, **5**, 135.

<sup>16</sup> *Ibid.*, *J. gen. Physiol.*, 1925, **8**, 33.

### Summary.

1. Careful measurements of the adsorption of hydrated cupric ferrocyanide for sucrose and for NaCl and  $\text{Na}_2\text{SO}_4$ , alone and in presence of sucrose, have been performed.

2. The apparent adsorption of sucrose is negative and results indicate that no sucrose is adsorbed by the gel, the hydration of which remains constant, independent of sucrose concentration.

3. This bound water is regarded as being partly polarised on the gel surface and partly imbibed between the crystallites. Only the former depends on the activity of the water in the solution.

4. NaCl and  $\text{Na}_2\text{SO}_4$  are also negatively adsorbed, but at low concentration there is evidence of positive adsorption. Slight cationic exchange occurs between the gel and the salts, but no anionic exchange has been detected.

5. In presence of sucrose, the negative adsorption of the salts is diminished, indicating that the imbibed water may be available to the ions though not to sucrose. Hence sucrose cannot be used to measure the hydration of the gel in presence of the salts.

6. A new form of cupric ferrocyanide is recorded.

We wish to record our thanks to Dr. E. Heymann and Dr. J. S. Anderson for very helpful discussion.

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## THE CATALYTIC EXCHANGE OF HYDROGEN ATOMS BETWEEN MOLECULAR DEUTERIUM AND PROPANE AND BUTANE.

BY A. FARKAS.

*Received 30th November, 1939.*

Examples of the catalytic exchange of hydrogen atoms between molecular hydrogen and saturated hydrocarbons were first given by Taylor and his collaborators.<sup>1,2</sup> According to these authors, methane, ethane and propane will exchange on a nickel-kieselguhr catalyst at temperatures above 180°, 110° and 65° C. respectively at pressures around half an atmosphere, within some hours. Later it was shown by Farkas and Farkas<sup>3</sup> that both cyclohexane and *n*-hexane will undergo exchange reactions on a platinum catalyst at temperatures slightly above room temperature. The present paper refers to experiments on the exchange of propane and butane on the same type of catalyst.

### Experimental Method.

The experimental arrangement was the same as used in previous investigations.<sup>4</sup> It consisted of a reaction vessel containing a platinised platinum foil catalyst (10 × 18 mm.), a U-tube cooled to -40° to -80° C.

<sup>1</sup> Morikawa, Benedict and Taylor, *J. Am. Chem. Soc.*, 1936, 58, 1445, 1795.

<sup>2</sup> Morikawa, Trenner and Taylor, *ibid.*, 1936, 59, 1103.

<sup>3</sup> Farkas and Farkas, *Trans. Faraday Soc.*, 1939, 35, 917.

<sup>4</sup> Farkas and Farkas, *J. Am. Chem. Soc.*, 1938, 60, 22.

and a mercury manometer. The butane used was prepared by hydrogenating *n*-butene, which in turn was prepared from *n*-butyl alcohol. The propane was obtained by hydrogenating acetone.<sup>5</sup> In one experiment ethane was used. It was produced from ethylene by hydrogenation.

### Exchange of Butane.

A typical exchange experiment (No. 11) between 16 mm. butane and 30 mm. deuterium at 67° is shown in Fig. 1, curve 11. In the first 40 minutes of the experiment the butane was condensed in a side tube. The absence of any decrease in the D-content indicated clearly that the catalyst did not contain appreciable amounts of light hydrogen. As soon as the butane was evaporated, a rapid exchange set in, and the D-content of the heavy hydrogen fell in 33 minutes from 96 % to 18 %.

Allowing for the relative amounts of hydrogen and butane in the reaction mixture and assuming that all ten hydrogen atoms of the butane molecule participate in the exchange, a D-content of 29.4 % in the butane can be calculated from the decrease of the D-content in the heavy hydrogen. This figure corresponds to a distribution ratio of

$$(H/D)_{\text{hydrogen}} \cdot (D/H)_{\text{butane}} = \frac{82}{18} \cdot \frac{29.4}{70.6} = 1.89$$

which agrees with that derived from theoretical considerations<sup>6</sup> and from exchange experiments with other hydrocarbons.<sup>2, 3</sup> This proves that in

fact all hydrogen atoms of the butane molecule participate equally in the exchange.

In experiment No. 12, 14 mm. butane containing 29 % D obtained in the above experiment was brought into contact with 20 mm. fresh D at 66° C. As shown by curve 12 in Fig. 1, the exchange proceeded at a similar speed as in the previous experiment. These experiments proved definitely that

the observed exchange involved actually butane and not butene, which might be said to have been contained in it as impurity, as any such butene would have been hydrogenated in the previous experiment. The final D-

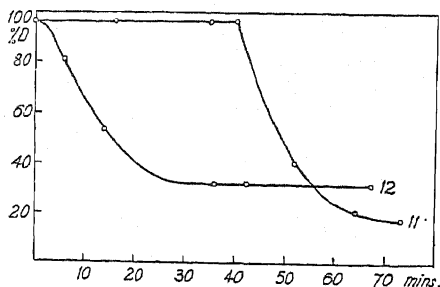


FIG. 1.

Expt. 11: 16 mm. Butane + 30 mm. D<sub>2</sub> at 67° C.

Expt. 12: 14 mm. Butane (29% D) + 20 mm. D<sub>2</sub> at 66° C.

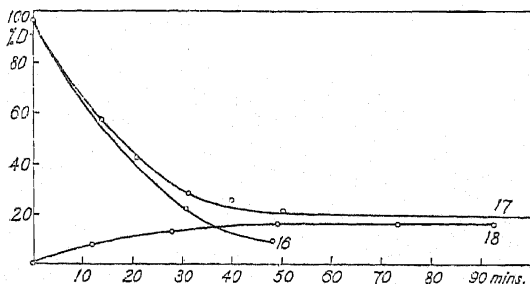


FIG. 2.

Expt. 16: 28 mm. Butane + 28 mm. D<sub>2</sub> at 26° C.

Expt. 17: 27 mm. Butane (18% D) + 27 mm. D<sub>2</sub> at 26° C.

Expt. 18: 27 mm. Butane (34% D) + 19 mm. H<sub>2</sub> at 26° C.

<sup>5</sup> Farkas and Farkas, *J. Am. Chem. Soc.*, 1939, 61, 1336.

<sup>6</sup> Wirtz, *Z. Elektrochemie*, 1937, 43, 662.

content of 31 % in the heavy hydrogen corresponds to a D-content of 48 % in the butane and to a distribution ratio of  $69/31 \cdot 48/52 = 2.05$ , which is very close to the value given above.

On a freshly platinised catalyst (Expt. No. 16) a rapid exchange occurs at room temperature, as is shown by Fig. 2. Curve 16 represents the

TABLE I.

TABLE I.—EXPT. 19, 21 MM.  $H_2$  + 26 MM. BUTANE CONTAINING 32 % D. TEMPERATURE 26° C.

Time.	D-content in %.	
	In Hydrogen.	In Butane (Calculated).
0 mins.	0.0	32.0
14 "	5.4	—
21 "	7.8	—
31 "	9.3	30.5
50 "	11.8	—
78 "	13.0	—
48 hours	15.0	29.6

interaction of 28 mm. of butane and 28 mm. of deuterium (96 % D) and curve 17, that of 27 mm. deuterium (97 %) and 27 mm. of butane containing 18 % D obtained in the previous experiment. In experiment No. 17, the D-content in the heavy hydrogen fell to 17.5 % after 19 hours, at which time the equilibrium must have been reached. As in the course of this exchange the D-content of the butane rose to 34 %, the equilibrium corresponds to a distribution ratio of

$$82.5/17.5 \cdot 34/66 = 2.43.$$

In experiment No. 18, 27 mm. butane containing 34 % D were brought into contact with 19 mm.  $H_2$ . In the first 35 minutes the butane was condensed in a side tube and during this time no increase in the D-content appeared in the hydrogen. The progress of the exchange reaction after the evaporation of the butane is shown by curve 18, Fig. 2.

The progress of experiment No. 19 is shown in Table I. The equilibrium corresponds to a distribution ratio of  $85/15 \cdot 29.6/40.4 = 2.38$ .

The progress of the exchange reaction with time can be satisfactorily represented by the formula

$$D_t - D_\infty = (D_0 - D_\infty) e^{-kt} \quad (1)$$

where  $D_0$ ,  $D_t$  and  $D_\infty$  designate the D-content of the heavy hydrogen at the time  $t=0$ ,  $t$  and  $t=\infty$  (i.e., at equilibrium), as is shown by Fig. 3, in which

$$\log [D_t - D_\infty] / (D_0 - D_\infty)$$

is plotted against the time.

The dependence of the rate of exchange on temperature is shown in Table II for three series of experiments. The half periods of exchange listed in this table were determined on the basis of formula (1). The apparent energy of activation of the exchange reaction as calculated from its dependence on temperature is 26.3 k.cal. in the temperature region 26°-41° C. and falls to 11.0 k.cal. at 77°-95° C.

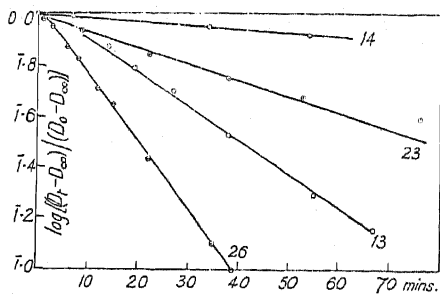


FIG. 3.

Expt. 13: 28 mm. Butane + 29 mm.  $D_2$  at 41° C.

Expt. 14: 22 mm. Butane + 25 mm.  $D_2$  at 26° C.

Expt. 23: 17 mm. Propane (27% D) + 29 mm.  $D_2$  at 51° C.

Expt. 26: 32 mm. Butane + 33 mm.  $D_2$  at 72° C.

TABLE II.

No.	Deuterium (mm.).	Butane (mm.).	Temp. (°C.).	Half Period (mins.).	Energy of Activation (k.cal.).
13	29	28	41	25	26.3
14	25	22	26	210	
14a	25	22	59	10.5	17.9
28	26	26.5	27	120	15.7
27	26	26	52	16	
40	22	21	77	32	11.0
39	20	21	95	16	

## Exchange of Propane.

Two typical exchange experiments with propane are shown in Fig. 4. Curve 21 (Expt. No. 21) refers to an experiment in which the catalyst was in a very active state. In the 64th minute the temperature of the catalyst was raised from 26° to 53°. In the course of the exchange the D-content of the hydrogen fell from 98 % to 15.2 %. Curve 25 represents an experiment (No. 25) carried out at 73° on the same catalyst in a somewhat less active state. It will be seen that while the decrease in the D-content was very slight in the course of the first 37 minutes, during which the propane was kept condensed in a side tube, a rapid exchange set in as soon as the propane was admitted to the deuterium in the reaction vessel.

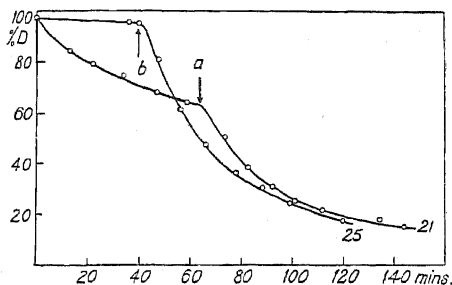


Fig. 4.

Expt. 21: 17.5 mm. Propane + 23 mm. D<sub>2</sub>.

At *a* the temperature was raised from 26 to 53° C.

Expt. 25: 28 mm. Propane + 27 mm. D<sub>2</sub> at 73° C. Propane added at *b*.

If it is assumed again that all hydrogen atoms in the propane molecule participate in the exchange from the results of experiment No. 21, a final D-content of 27.2 % can be calculated in the propane. This figure corresponds to a distribution ratio of  $84.8/15.2 \cdot 27.2/72.8 = 2.08$  at 53°. Probably equilibrium was not completely reached in this experiment and therefore the actual value of the distribution coefficient should be slightly higher. Morikawa, Turner and Taylor<sup>2</sup> found for the equilibrium constant for this exchange reaction  $K = 2.57$  at 80°. The agreement with this figure can be regarded as sufficiently good.

TABLE III.

No.	Deuterium (mm.).	Propane (mm.).	Temp. (°C.).	Half Period (mins.).	Energy of Activation (k.cal.).
21	23	21.5	26	90	11.6
21a	23	21.5	53	18	
31	22	19	40	160	10.2
31a	22	19	73	33	
38	22	24	97	67	8.8
37	21	20	126	28	

The dependence of the rate of exchange on temperature is given in Table III, together with the energies of activation. It is possible that in experiment 21, some deactivation of the catalyst occurred by heating it to 53°, so the obtained energy of activation appears smaller than it actually is.

The rate of exchange of propane has been compared with that of butane at 26° and 95°, and with that of ethane at 72°. The results obtained are listed in Table IV. It will be noted that while exchange of butane proceeds about 4 times faster in the temperature region 26° to 97° than that of propane, that of ethane is 36 times smaller.

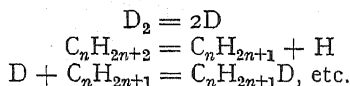
TABLE IV.

No.	Pressure (mm.).		Temperature (°C.).	Half Period (mins.).
	Deuterium.	Hydrocarbon.		
20	19	25 Butane	26	25
21	23	21.5 Propane	26	90
38	22	24 Propane	97	67
39*	21	20 Butane	97	14.5
25	27	28 Propane	72	20
24	28	24 Ethane	72	720

\* Half period calculated from experiment No. 39 at 95°.

These results indicate that the rate of exchange on a platinum catalyst increases in the series  $C_2H_6 < C_3H_8 < C_4H_{10}$ . This series is in agreement with the rate of exchange observed with hexane,<sup>3</sup> with the series  $CH_4 < C_2H_6 < C_3H_8$  obtained by Taylor and his collaborators for the exchange on a nickel catalyst and also with the general stability of these hydrocarbons.

The nature of the hydrocarbon excludes the possibility of associative mechanism and the simplest mechanism for this type of exchange reaction is the dissociative mechanism



This mechanism was originally suggested for the exchange reaction for ethylene<sup>4, 7</sup> and later applied to the reaction of a number of other unsaturated and saturated hydrocarbons.<sup>1, 2, 3, 8, 9</sup>

In the light of the present experiments, two recent papers deserve reconsideration. The first<sup>5</sup> refers to the catalytic interaction of acetone and heavy hydrogen. In this reaction an exchange was observed which was attributed to a reaction involving acetone. As in the interaction of acetone and hydrogen propane is formed, one would think that in the exchange reaction actually the propane might have been involved also. A comparison of the present results with the previous experiments shows, however, that a reasonably fast exchange of propane can be found at low temperature only on a very active freshly prepared catalyst. Since the catalyst used in the experiments with acetone was only an ordinary catalyst, it would not be expected to be sufficiently active to cause an exchange with propane.

<sup>7</sup> Farkas, Farkas and Rideal, *Proc. Roy. Soc. A.*, 1934, 146, 630.

<sup>8</sup> Farkas and Farkas, *Trans. Faraday Soc.*, 1937, 33, 827.

<sup>9</sup> Farkas, *ibid.*, 1939, 35, 906.

In the second paper,<sup>10</sup> the hydrogenation and exchange of propylene and butene on a nickel catalyst is described by Twigg. He thought that the participation of all hydrogen atoms of the hydrocarbons molecules in the exchange is inconsistent with the dissociative mechanism and can be explained only by the associative mechanism. The present experiments, however, definitely establish the exchange of all hydrogen atoms in hydrocarbons of such a type that the associative mechanism cannot be operative at all.

### Summary.

The exchange of hydrogen atoms between molecular hydrogen and propane and butane on a Pt catalyst has been investigated at pressures around 40 to 50 mm. at 26 to 126° C. These hydrocarbons exchange all their hydrogen atoms in a reversible manner. On a very active catalyst the exchange takes place readily at room temperature. The exchange of propane is 4 to 5 times slower than that of butane but 36 times faster than that of ethane.

The energy of activation for the exchange of butane is 26 k.cal. in the region 26°-41° C. and falls to 11 k.cal. at 77°-95° C. The energy of activation for the exchange of propane is 12.9 k.cal. It is suggested that the exchange reaction proceeds by the dissociative mechanism.

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<sup>10</sup> Twigg, *Trans. Faraday Soc.*, 1939, **35**, 934.

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## CALCULATION OF THE THIRD LAW ENTROPY OF ETHYL CHLORIDE.

By J. W. LINNETT.

*Received 20th December, 1939.*

A comparison of the observed values for the thermodynamic quantities, entropy and heat capacity, with those obtained by theoretical calculations has been used in attempts to determine whether or not, in certain molecules, there is free internal rotation of one part of the molecule with respect to another part. In some cases, such as that of ethane, a quite definite decision has been reached. If the entropy of ethyl chloride could be obtained and if the necessary calculations could be made, it should be possible to determine whether free rotation of the methyl group occurs in this molecule.

The third law entropy of ethyl chloride has not been determined directly, but a value should be obtainable from data on the equilibrium in the system  $C_2H_5Cl = C_2H_4 + HCl$ , since the entropies of ethylene and of hydrogen chloride are known with considerable certainty. Data on this system have been obtained by Rudkovskii, Trifel and Frost,<sup>1</sup> who studied the equilibrium over the range 170° to 230° C. The standard entropy change for this reaction may, therefore, be estimated and from it the third law entropy of ethyl chloride at 200° C. obtained.

<sup>1</sup> Rudkovskii, Trifel and Frost, *Ukrain. Khim. Zhem.*, 1935, **10**, 277.



For the theoretical calculation of the entropy it is necessary to know (a) the three principal moments of inertia of the ethyl chloride molecule, and (b) the fundamental vibration frequencies of the molecule. The only serious uncertainty in the dimensions of this molecule is in the carbon-chlorine distance, so that in the present paper the moments of inertia have been calculated for several values of this bond length. From the observed Raman and infra-red spectra of ethyl chloride, and by comparison with the frequencies of related molecules, it has been possible to obtain a set of fundamental vibration frequencies which are sufficiently accurate for the present purpose.

The calculation of the vibrational contribution to the entropy was made with the aid of tables compiled by Cross and Crawford, the vibrations being assumed to be of a simple harmonic character. The translational and rotational contributions were calculated using the usual formulæ, assuming the rotational levels to be fully excited. All the entropies calculated refer to the standard state.

### Entropy of Hydrogen Chloride.

The third law entropy of hydrogen chloride has been determined experimentally by Giauque and Overstreet,<sup>2</sup> who give 44.5 cal./degree C. as the value for this quantity at 298° K. Since the internuclear distance, vibration frequency and isotopic constitution of this molecule are known very accurately the entropy may be calculated with a certainty that is greater than that of the experimental results. Taking the inter-nuclear distance as 1.272 Å. and the vibration frequency as 2989 cm.<sup>-1</sup>, the entropy is calculated to have the values listed in Table I. The figure, 44.62, for the entropy at 298° K. agrees closely with the experimentally determined value.

### Entropy of Ethylene.

Smith and Vaughan<sup>3</sup> have calculated the entropy of ethylene, giving the value at 298° K. as 52.55 cal./degree C. In this paper the entropy has been calculated using rather different values for the constants. The moments of inertia of the ethylene molecule have been determined recently by Thompson<sup>4</sup> who gives the values:  $33.197 \times 10^{-40}$ ,  $27.48 \times 10^{-40}$ , and  $5.714 \times 10^{-40}$  g./cm.<sup>2</sup>. These results agree closely with the earlier values of Badger<sup>5</sup> determined by a quite independent method.

There is still some uncertainty regarding the vibration frequencies of ethylene. Smith and Vaughan employed the assignment suggested by Bonner.<sup>6</sup> In the present case the following frequencies have been used: Planar vibrations: Raman active: 3019, 1623 and 1342; 3076 and 1240; Infra-red active: 2988 and 1444; 3107 and 950; Non-planar vibrations: Raman active: 1110; Infra-red active: 940; Inactive: 740 cm.<sup>-1</sup>. This assignment explains all the Raman and infra-red spectral data and has the advantage that it reproduces the observed heat capacities much more satisfactorily than does the assignment due to Bonner. For this reason, particularly, it has been used in the entropy

<sup>2</sup> Giauque and Overstreet, *J.A.C.S.*, 1932, **54**, 1742.

<sup>3</sup> Smith and Vaughan, *J. Chem. Physics*, 1935, **3**, 341.

<sup>4</sup> Thompson, *Trans. Faraday Soc.*, 1939, **35**, 697.

<sup>5</sup> Badger, *Physic. Rev.*, 1934, **45**, 648.

<sup>6</sup> Bonner, *J.A.C.S.*, 1936, **58**, 34.

calculations. The calculated values of the translational and rotational entropy, the vibrational entropy, and the total entropy are given in Table I. It will be noted that, in this table, the entropy at 298° K. is given as 52.41, which does not differ greatly from the value of Smith and Vaughan. In the last column of Table I are given the sums of the entropies of hydrogen chloride and ethylene at the various temperatures listed in the first column.

TABLE I.—THE CALCULATED ENTROPIES OF GASEOUS HYDROGEN CHLORIDE AND ETHYLENE.

T(°K.).	SHCl.	Ethylene.			SHCl + SC <sub>2</sub> H <sub>4</sub> .
		S <sub>t</sub> + r.	S <sub>vib.</sub>	S <sub>total</sub> .	
273	44.01	51.08	0.47	51.55	95.56
298	44.62	51.77	0.64	52.41	97.03
323	45.18	52.51	0.86	53.37	98.55
373	46.18	53.56	1.37	54.93	101.11
423	47.06	54.56	1.97	56.53	103.59
473	47.84	55.44	2.63	58.07	105.91
523	48.54	56.24	3.33	59.57	108.11
573	49.18	56.97	4.05	61.02	110.20

### Entropy of Ethyl Chloride.

**The Moments of Inertia.** As has been remarked previously, the difficulty that arises in the calculation of the principal moments of inertia of this molecule is the fixing of the carbon-chlorine interatomic distance. The value of this distance in methyl chloride is uncertain as has been indicated by Sutherland.<sup>7</sup> The distance in the ethyl compound has been determined by electron diffraction. An early determination by Brú<sup>8</sup> gave the internuclear distance as  $1.81 \pm 0.08$  Å., but, more recently, Beach and Stevenson<sup>9</sup> have re-examined the problem and give the result  $1.76 \pm 0.02$  Å. Because of this uncertainty, calculations have been made assuming the bond length to be (a) 1.70, (b) 1.75, and (c) 1.80 Å. The carbon-carbon distance has been taken to be 1.54, and the carbon-hydrogen distance 1.093 Å. All the angles have been assumed to be tetrahedral. These assumed dimensions cannot differ greatly from those existing. The results for the principal moments of inertia are: (a) Cl<sup>35</sup>: 16.23, 95.41 and 85.60; Cl<sup>37</sup>: 16.26, 97.24 and 87.40; (b) Cl<sup>35</sup>: 16.44, 98.63 and 88.62; Cl<sup>37</sup>: 16.46, 100.54 and 90.50; (c) Cl<sup>35</sup>: 16.63, 101.93 and 91.72; Cl<sup>37</sup>: 16.66, 103.92 and 93.68. All the above figures are given in atomic weight and Angstrom units.

**The Vibration Frequencies.** The infra-red absorption spectrum of ethyl chloride has been examined by Cross and Daniels.<sup>10</sup> At frequencies below 1500 cm.<sup>-1</sup> bands have been observed at ca. 750, 790, 975, ca. 1050, ca. 1090, ca. 1120, 1400 and 1455 cm.<sup>-1</sup>. The early work on the Raman spectrum of ethyl chloride is summarised in Kohlrausch's *Smekel-Raman Effekt*. The spectrum has also been examined by Harkness and Haines.<sup>11</sup>

<sup>7</sup> Sutherland, *Trans. Faraday Soc.*, 1938, 34, 325.

<sup>8</sup> Brú, *Anales soc. espan. fis quim.*, 1933, 31, 115.

<sup>9</sup> Beach and Stevenson, *J.A.C.S.*, 1939, 61, 2643.

<sup>10</sup> Cross and Daniels, *J. Chem. Physics*, 1933, 1, 52.

<sup>11</sup> Harkness and Haines, *J.A.C.S.*, 1932, 54, 3920.

The Raman frequencies are : 337, 438, 655, 966, 1071, 1276, 1448, 2875, 2930 and 2966  $\text{cm}^{-1}$ .

Ethyl chloride has seventeen distinct fundamental vibrations in addition to the possible torsional oscillation. Of these eighteen motions eleven may be regarded as symmetrical and seven as antisymmetrical. From the available spectroscopic data it is quite impossible to make an unambiguous assignment of the fundamental frequencies. By analogy with similar molecules, however, it is possible to fix the probable magnitudes of the frequencies and then by comparison with the spectroscopic data to obtain a list of fundamental frequencies accurate enough for the present calculations.

TABLE II.

Group Vibrating.	Symmetry.	Description of Vibration.	Related Vibration of Simpler Molecules.	Approx. Frequency.
Framework	S	C—C valency	C—C valency	950
	S	C—Cl valency	C—Cl valency	700
	S	C—C—Cl deform.	C—C—Cl deform.	350
Methyl	S	C—H valency	C—H Symm. valency	2940
	S	C—H valency	C—H Degenerate valency	3050
	A	C—H valency		
	S	CH <sub>3</sub> Symm. deform.	CH <sub>3</sub> Symm. deform.	1350
	S	CH <sub>3</sub> deform.	CH <sub>3</sub> Degenerate deform.	1450
	S	CH <sub>3</sub> deform.		
	S	CH <sub>3</sub> deform.	CH <sub>3</sub> Degenerate deform.	1000
	A	CH <sub>3</sub> deform.		
	A	CH <sub>3</sub> deform.		
	A	CH <sub>3</sub> deform.		
Methylene	S	C—H valency	C—H valency (SS)*	2950
	A	C—H valency	C—H valency (SA)	3050
	S	CH <sub>2</sub> deform.	CH <sub>2</sub> deform. (SS)	1400
	S	CH <sub>2</sub> bending †	CH <sub>2</sub> bending (AS)	1100
	A	CH <sub>2</sub> rocking †	CH <sub>2</sub> rocking (SA)	1050
	A	CH <sub>2</sub> twisting †	CH <sub>2</sub> twisting (AA)	850
	A	CH <sub>2</sub> twisting †		

\* The letters S and A indicate the symmetry of the vibration in the molecules of the type Y . CH<sub>2</sub> . Y with respect to the two planes of symmetry.

† For the significance of the terms bending, rocking and twisting, see *J. Chem. Physics*, 1938, 6, 695.

The vibrations of the ethyl chloride molecule may be divided into three sets : (1) Vibrations of the C—C—Cl framework, (2) Vibrations of the methyl group, (3) Vibrations of the methylene group. The torsional oscillation is not included in the present considerations. The vibrations of set (1) may be related to the vibrations of a non-linear triatomic molecule, those of set (2) to the vibrations of the methyl group in the methyl halides, CH<sub>3</sub>X, and those of set (3) to the vibrations of the methylene group in the methylene halides, Y . CH<sub>2</sub> . Y. This correspondence between the vibrations of the ethyl chloride molecule and the vibrations of the more simple molecules is shown diagrammatically in Table II. The approximate magnitudes of the vibration frequencies for the simpler

molecules are given in the last column. From the above correspondence a rough set of frequencies for the ethyl chloride molecule is deduced to be: Five of 3000, two of 1450, 1400, 1350, 1100, 1050, two of 1000, 950, 850, 700, and 350  $\text{cm}^{-1}$ . Combining these with the frequencies observed in the Raman and infra-red spectra we are led to the following list of frequencies: Five of 3000, two of 1450, 1400, 1290, 1120, 1070, 1050 and 1000, 970, 790, 655 and 337  $\text{cm}^{-1}$ . These frequencies have been used in calculating the vibrational contribution to the entropy. It is not suggested that the above assignment would be sufficiently accurate for general use, but it is certainly good enough for the present entropy calculations, and will lead to an error in the vibrational contribution at 200° C. of not more than 0.5 cal. per g./mol.°C.

**Calculation of the Entropy of Ethyl Chloride.** Using the above values for the moments of inertia and the vibration frequencies calculations of the entropy have been made for the two extreme conditions, namely (1) completely free rotation of the methyl group, and (2) completely restricted rotation of the methyl group, excluding even the contribution to the entropy arising from a torsional oscillation. Assumption of a torsional oscillation or a partially restricted rotation would give a value between these limits. For the calculation of the rotational entropy when free internal rotation of the methyl group is involved the treatment given by Kassel<sup>12</sup> has been employed. The values calculated for the entropy of ethyl chloride are given in Table III.

TABLE III.—CALCULATED VALUES OF THE ENTROPY OF ETHYL CHLORIDE.

T(°K).	Completely Restricted Rotation.			Completely Free Rotation.		
	$r_{\text{CCl}} = 1.70$ .	1.75.	1.80.	1.70	1.75.	1.80 A.
273	62.94	63.02	63.10	66.29	66.37	66.45
298	64.07	64.15	64.23	67.51	67.59	67.67
303	65.18	65.26	65.33	68.69	68.77	68.85
373	67.35	67.43	67.50	71.00	71.08	71.16
423	69.47	69.55	69.62	73.25	73.33	73.41
473	71.53	71.61	71.69	75.42	75.50	75.58
523	73.54	73.62	73.70	77.53	77.61	77.69
573	75.51	75.59	75.67	79.59	79.67	79.75

### The Observed Change in Entropy for $\text{C}_2\text{H}_4 + \text{HCl} = \text{C}_2\text{H}_5\text{Cl}$ .

The equilibrium in the system ethyl chloride, ethylene and hydrogen chloride has been investigated by Rudkovskii, Trifel and Frost. They studied this system at 170°, 200° and 230°, the rate of attainment of the equilibrium being accelerated by the presence of bismuth chloride on silica. They obtained the following expression for  $K_p$  as a function of the absolute temperature:

$$\log K_p = 4.96 - \frac{2935}{T}.$$

The above value of  $K_p$  is obtained from a process occurring at constant pressure, and so the entropy change of  $-22.7$  cal. per °C. calculated from it represents the change in entropy on passing from a mixture of 1 g. molecule of ethylene and 1 g. molecule of hydrogen chloride at

<sup>12</sup> Kassel, *J. Chem. Physics*, 1936, 4, 276.

atmospheric pressure and 200° C. to 1 g. molecule of ethyl chloride at atmospheric pressure and 200° C. To obtain the standard entropy change,  $S_{C_2H_4} + S_{HCl} - S_{C_2H_5Cl}$ , it is necessary to introduce a correction for the entropy change on mixing the ethylene and hydrogen chloride. This will make  $S_{C_2H_4} + S_{HCl} - S_{C_2H_5Cl}$  equal to 19.9 cal. per °C.

### Discussion.

If 19.9 is subtracted from the sum of the entropies of hydrogen chloride and ethylene at 200° C., the value obtained for the entropy of ethyl chloride at this temperature is 86. Comparing this value with those given in Table III, it will be seen to be considerably higher even than the value calculated assuming free rotation. In this case the discrepancy is about 10.4 entropy units, while for restricted rotation the discrepancy is 14.3 units. Both these errors are certainly outside that which could possibly arise in the theoretical calculations. It must be concluded, therefore, that the experimental value for the entropy change is unsatisfactory. In Table IV are given the calculated values for the entropy change.

TABLE IV.—CALCULATED VALUES OF THE STANDARD ENTROPY CHANGE FOR THE REACTION  $C_2H_5Cl = C_2H_4 + HCl$ .

T(°K).	Completely Restricted Rotation.			Completely Free Rotation.		
	$r_{CCl} = 1.70$ .	1.75.	1.80.	1.70.	1.75.	1.80 A.
273	32.62	32.54	32.46	29.27	29.19	29.11
298	32.96	32.88	32.80	29.52	29.44	29.36
323	33.37	33.29	33.22	29.86	29.78	29.70
373	33.76	33.68	33.61	30.11	30.03	29.95
423	34.12	34.04	33.97	30.34	30.26	30.18
473	34.38	34.30	34.22	30.49	30.41	30.33
523	34.57	34.49	34.41	30.58	30.50	30.42
573	34.69	34.61	34.53	30.61	30.53	30.45

The error in the experimental value of the entropy change may arise because of small errors in the values of  $K_p$  at each of the temperatures studied causing a line with the incorrect slope to be drawn when  $\log K_p$  is plotted against the reciprocal of the absolute temperature. Alternatively the equilibrium constants at the three temperatures may be badly in error because of some unnoticed effect, such as, for example, a side reaction. It would certainly seem that little effort was made to prove that the simple reversible reaction  $C_2H_5Cl = C_2H_4 + HCl$  was all that was taking place in the system examined by Rudkovskii, Trifel and Frost. In favour of the first possibility it is to be observed that, though the individual results at 230° C. are quite consistent, those at the lower temperatures show considerable variation.

The difference between the entropy change calculated assuming free rotation and that calculated assuming completely restricted rotation is approximately 4 entropy units. This would mean a difference for the two extreme conditions in the temperature independent term of the expression for  $\log K_p$  of about one unit. It must be concluded, therefore, that if accurate data were available on the equilibrium in this system it would be possible to obtain information regarding the motion of the methyl group in the ethyl chloride molecule.

## Summary.

The entropy of ethyl chloride between 273° and 573° K. has been calculated both assuming restricted and assuming free rotation of the methyl group. By combining these results with the calculated entropies of ethylene and hydrogen chloride the entropy change for the reaction  $C_2H_5Cl = C_2H_4 + HCl$  has been calculated for the same range of temperature. From data on the equilibrium in the above system it has been possible to obtain an experimental value for the entropy change at 200° C. It is found that the calculated and experimental values at this temperature are widely different, and it is concluded that the experimental result is in error. The practicability of using the entropy change for this reaction to obtain information regarding the problem of internal rotation in ethyl chloride is discussed.

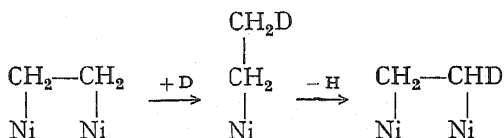
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## THE CHEMISORPTION OF OLEFINS ON NICKEL.

BY G. H. TWIGG AND ERIC K. RIDEAL.

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Recent investigations which have been carried out on the exchange reactions between olefins and deuterium<sup>1</sup> have indicated that exchange proceeds through an associative mechanism, e.g.



This implies that when the olefine is chemisorbed on the catalyst, the double bond is opened and attachment takes place between the two carbon atoms of the double bond and two nickel atoms. It is therefore of interest to calculate how ethylene and higher olefins fit in this manner to a nickel surface.

The first calculation is concerned with the fitting of the olefine molecule between the two nickel atoms (Figs. 1 (a) and (b)). The ethylene molecule is used for these calculations as the interatomic distances are not appreciably affected by substitution of alkyl groups for hydrogen atoms on the double bond. The ethylene then fits to the catalyst as shown in Figs. 1 (a) and (b).

The following values for the lengths of the bonds are used:—

(a) Ni—Ni 2.47 Å. (Davy, *Physic. Rev.*, 1925, **25**, 753).

(b) Ni—C 1.82 Å. (Crawford and Cross, *J. Chem. Physics*, 1938, **6**, 525).

(c) C—C 1.52 Å. (Brockway, *Rev. Mod. Physics*, 1936, **8**, 261).

Since the nickel crystal has a face-centred cubic structure, there are two nickel-nickel distances to be considered, the distance of closest

<sup>1</sup> Twigg and Rideal, *Proc. Roy. Soc., A*, 1939, **171**, 55; Twigg, *Trans. Faraday Soc.*, 1939, **35**, 934.

packing 2.47 Å. and the unit cell side 3.50 Å. (Davy, *loc. cit.*). It can be shown that the distance 3.50 Å is too great for adsorption in the manner postulated above; adsorption must therefore take place on the 2.47 Å. distance. The nickel-carbon distance is not easy to determine; it is taken here as being equal to the Ni—C distance in nickel carbonyl  $\text{Ni}(\text{CO})_4$ . The C—C distance is taken as the single bond distance in paraffins. From Fig. 1 (a) it is seen that  $a = c - 2b \cos \theta$  and substituting for  $a$ ,  $b$ , and  $c$ , we find  $\theta = 105^\circ 4'$ , in place of the tetrahedral angle  $109^\circ 28'$  which one would expect. Thus by a slight decrease of the angle, the molecule fits very well to the surface. The change in the

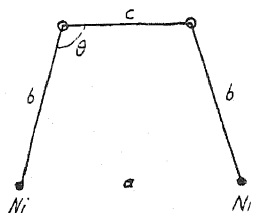


FIG. 1a.

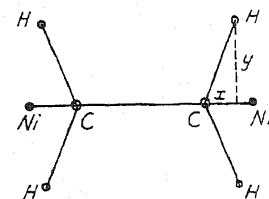


FIG. 1b.

0 1 2 3  
Scale in Å.

FIG. 1.—(a) Chemisorbed ethylene molecule—side view.

(b) Chemisorbed ethylene molecule—plan.

angle  $\theta$  from the tetrahedral angle required for a good fit will actually be much less, as the molecule can accommodate itself by twisting slightly so that the C—C axis lies at a small angle to the Ni—Ni axis. It is also possible that the process of forming an active catalyst, by oxidation followed by reduction, causes an increase in the interatomic distance. The promotion of nickel catalysts by oxygen<sup>2</sup> may be due to the oxygen atoms maintaining the crystal lattice in an expanded state.

The interatomic distance of the catalyst atoms appears to be an important factor in determining the activity of the catalyst, whether on account of the fitting of the adsorbed molecules as discussed above or because of distortion of the lattice changing the properties of the catalyst atoms. The experiments of Maxted and co-workers<sup>3</sup> suggest that the activity of a catalyst is not due to isolated active atoms, but is present

in relatively large areas of the catalyst. The low temperature at which activation of a nickel catalyst by oxidation and reduction ( $90^\circ \text{C}$ . in one experiment here) can be brought about militates against the view that isolated highly unsaturated atoms are being produced. Activation is then probably due, not only to an increase in area, but also to an alteration in interatomic distance.

In the chemisorption of olefins in the manner described above, if the angles between the valences were the tetrahedral angles, the distance between the nickel atoms would have to be 2.73 Å. This may be taken as approximately an upper limit for the catalyst spacing. This agrees with the fact that catalysts active in hydrogenation have interatomic distances (distances of closest approach) lying between 2.47 Å. and 2.54 Å. (Fe, Ni, Co, Cu) and between 2.7 Å. and 2.8 Å. (Pt, Pd). It is noteworthy that in the latter group where the distance is near the maximum, the form of the crystal lattice has become important, for only those metals with

<sup>2</sup> Juliard and Herbro, *Bull. Soc. Chim. Belgique*, 1938, 47, 717; Ablezova and Zellinskaja, *J. Physic. Chem. Russ.*, 1937, 9, 252.

<sup>3</sup> J.C.S., 1928, 1600.

interatomic distance between 2.7 Å. and 2.8 Å. which have also a face centred cubic lattice are active in hydrogenation. The greater activity of the face centred cubic crystal lattice was shown by Long, Frazer and Ott,<sup>4</sup> using alloys, to exist also for the other group of metals (Fe, Ni, Co, Cu).

That the fitting of the olefine to the catalyst surface is an important factor in such a reaction as hydrogenation seems to be shown by a preliminary experiment which was made with a tungsten catalyst.\* Under very rigorous conditions of cleanliness a wire catalyst was obtained very active for the para-hydrogen conversion (high temperature mechanism); the half life of the conversion was 5 minutes at  $-130^{\circ}\text{C}$ . A mixture of ethylene and hydrogen in contact with this catalyst showed no appreciable hydrogenation in half an hour during which the temperature of the catalyst was raised from  $-130^{\circ}\text{C}$ . to  $200^{\circ}\text{C}$ . The absence of reaction was due not to the inability of the catalyst to "activate" hydrogen, but to its inability to "activate" the ethylene which in turn seems bound up with the question of catalyst spacing.

The interatomic spacing must therefore exert a considerable influence on the ability of substances to catalyse reactions, though it is not suggested that this is the complete explanation.

The second calculation which has been made on the fitting of the olefine molecules to the surface concerns the interaction of neighbouring adsorbed molecules. Fig. 1 (b) represents a plane projection of the adsorbed ethylene molecule from a point above the surface.

The various distances and positions of the atoms have been calculated as follows. It has been assumed that all the angles between the valences of the carbon atoms are equal to the tetrahedral angle  $109^{\circ}28'$ . Then, if  $d$  is the length of the C—H bond,<sup>5</sup> 1.09 Å., the distance  $x$  is given by  $x = d/3 = 0.36$  Å., and the distance  $y$  by  $y = d\sqrt{2}/3 = 0.89$  Å.

In order to find out whether there is any interaction between the adsorbed olefine molecules, a plan of the adsorption on the 110 and 111 nickel planes has been drawn to scale (Fig. 2) using the above distances.

These planes were chosen for calculation since it has been shown (E. C. Williams, private communication) by means of experiments on evaporated nickel films, that the 110 nickel plane was catalytically active whereas the 100 plane was quite inactive.

The adsorption of ethylene on these two planes is demonstrated in Fig. 2; the effective sizes of the hydrogen atoms have been drawn in (full circles). The effective diameter of the hydrogen atom is taken as the diameter of the hydrogen molecule from viscosity, etc., measurements, less the internuclear distance. Taking the diameter<sup>6</sup> as 2.3 Å., and the internuclear distance<sup>7</sup> as 0.75 Å., this gives 0.78 Å. for the radius of the hydrogen atom. It will be seen that if the molecules are adsorbed on the 111 nickel plane (Fig. 2A), there is a certain amount of interaction between them, though this may not be sufficient to prevent ethylene covering the whole surface. On the other hand, if adsorption is on the 110 plane (Fig. 2B) there is no interaction between neighbouring adsorbed molecules, and the ethylene can easily cover the whole surface,

<sup>4</sup> J.A.C.S., 1934, 56, 1101.

\* This experiment was carried out in collaboration with Mr. D. D. Eley of this department.

<sup>5</sup> Sutherland, *Ann. Reports Chem. Soc.*, 1935, 33, 55.

<sup>6</sup> Farkas and Melville, *Experimental Methods in Gas Reactions*, p. 2, Macmillan & Co., London, 1939.

<sup>7</sup> Mecke, *Hand-Jahrbuch chem. Physik*, 1934, 9, 283.



as has been shown experimentally to be the case up to 160° C. (Twigg and Rideal).<sup>1</sup> There may, of course, be holes in the ethylene layer owing to the two-point contact required for the ethylene molecule.<sup>8</sup>

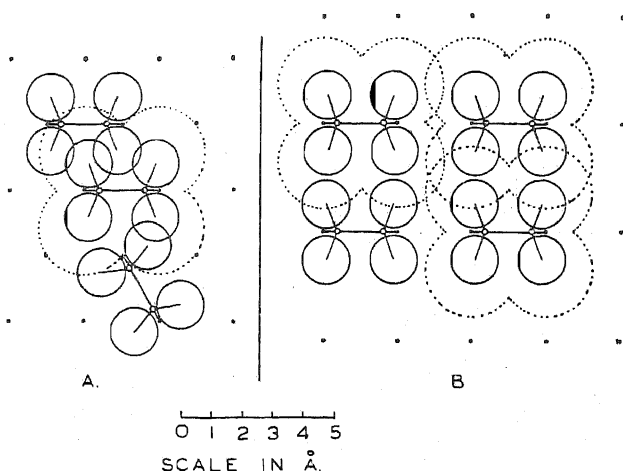


FIG. 2.—Plan of chemisorbed ethylene and methyl ethylenes on the nickel surface. A on the 111 plane. B on the 110 plane.

In the case of the methyl substituted ethylenes, interaction between neighbouring adsorbed molecules is very great, particularly if adsorption is on the 111 plane. The size of the  $-\text{CH}_3$  group is indicated by the dotted circles in Fig. 2. The diameter of the  $-\text{CH}_3$  group is taken as

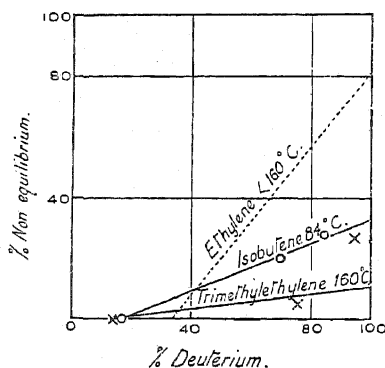


FIG. 3.—Equilibration of hydrogen during exchange reactions. x in presence of trimethylethylene at 160° C. o in presence of isobutene at 84° C.

the same as that of the methane molecule,<sup>9</sup> 3.06 Å. It will be seen that interaction between adsorbed methyl substituted ethylenes, even on the 110 plane would be so great that the whole surface could not be completely covered. It can also be seen from the fact that the dotted circles of the methyl groups overlap with the full circles of the hydrogen atoms, that even in the case of propylene with only one methyl group, there will be considerable interaction between the adsorbed molecules. This calculation then shows that despite their higher molecular weights, the substituted ethylenes should be less strongly adsorbed in quantity than ethylene itself, that they should be

unable to cover the whole surface and that there should be bare surface on which the equilibration reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  can take place. These conclusions were tested by means of the technique described previously (Twigg and Rideal).<sup>1</sup> The olefine and deuterium were allowed

<sup>8</sup> Cf. Roberts, *Proc. Roy. Soc., A*, 1935, 152, 464.

<sup>9</sup> Braune and Linke, *Z. physik. Chem., A*, 1930, 148, 195.

to interact on the catalyst, and the course of the exchange and equilibration reactions was followed simultaneously. The deuterium content  $\alpha$  of the hydrogen was graphed against the non-equilibrium content  $1 - \alpha$ . The results obtained are shown in Fig. 3.

Using ethylene, the points obtained at temperatures below  $160^{\circ}$  C. lie on the dotted line, showing that the ethylene covers the whole surface up to that temperature. Above that temperature the slope of the line decreases owing to displacement of the ethylene by hydrogen. With trimethylethylene at  $160^{\circ}$  C., however, the lowest line was obtained. Here equilibration is proceeding very fast, showing that the surface is considerably bare. The same phenomenon is illustrated by the other line which was obtained by using isobutene at as low as  $84^{\circ}$  C. The rapid equilibration confirms the conclusions drawn above, that the methyl substituted ethylenes, because of interaction between neighbouring adsorbed molecules, are unable to cover completely the whole catalyst surface.

### Summary.

Information derived from exchange reactions showed that olefines are chemisorbed to a nickel surface with opening of the double bond and adsorption to two nickel atoms. Calculations have been made which show that this mode of adsorption is possible with very little distortion of the adsorbed molecule. The effect of the interatomic spacing of the catalyst atoms is discussed and the view is advanced that this will be an important factor in the hydrogenation of double bonds where two point contact is required.

Calculations were also made qualitatively of the interaction between neighbouring adsorbed olefine molecules. It has been shown that for ethylene there is little or no interaction, especially when adsorption is on the 110 crystal plane; ethylene can therefore cover the whole catalyst surface. For the higher olefines, however, interaction is considerable and these molecules cannot cover the whole surface. The experimental evidence confirms these conclusions.

We have to thank the Carnegie Trust for a Fellowship to one of us (G. H. T.) and Dr. H. Melville for a microconductivity gauge.

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# ELASTIC RECOVERY AND PLASTIC FLOW IN RAW RUBBER.

By L. R. G. TRELOAR.

*Received 18th January, 1940.*

## 1. Purpose of the Work.

A satisfactory theory of the structure of raw rubber must be able to account for all the physical phenomena displayed by this material. It is of importance, therefore, that its physical behaviour should be carefully studied and described in the most direct and accurate manner possible. Experimental studies of this kind may also be of assistance in suggesting the most hopeful lines of approach to the theoretical study of the problem.\*

The first specific problem which appeared to require examination was that of the separation of the elastic and plastic effects which in general take place simultaneously when raw rubber is subjected to a deformation. The existing information on this subject is scanty. True, numerous studies of plasticity have been carried out, but these have been concerned almost entirely with masticated rubber, with which it is not proposed to deal here. Stress-strain curves for raw rubber at different temperatures have been given by Rosbaud and Schmid.<sup>1</sup> In contrast to those for vulcanised rubber, these show a great dependence on the temperature and on the rate of extension, effects which have generally been attributed to the occurrence of plastic flow, although the magnitude of the flow has not been determined. On the other hand, several workers, including in particular Feuchter,<sup>2</sup> have drawn attention to the fact that raw rubber, when stretched quickly to about 600 % elongation, recovers on warming practically to its original length, *i.e.*, there is no plastic flow in this case. Perhaps the most successful attempt to distinguish the plastic from the elastic deformation was made by Whitby<sup>3</sup> who clearly demonstrated the kind of difficulty encountered in an investigation of this kind. Whitby maintained specimens of raw rubber extended to a constant length for given times at various temperatures. They were then allowed to recover for several days at room temperature, until the length had ceased to change, but on subsequently raising the temperature to 100° C. a further contraction was observed. The "set" remaining after this treatment was regarded as a plastic deformation. This view will be shown not to have been entirely justified.

In the present work Whitby's methods have been taken as a starting-point, but greater care has been exercised in securing the complete removal of elastic strain. The data cover the following aspects of the behaviour of rubber:—

\* A review of existing knowledge of the physical properties of raw rubber is to be found in Chapter II, by G. S. Whitby, in *The Chemistry and Technology of Rubber* (New York, 1937).

<sup>1</sup> F. Rosbaud and E. Schmid, *Z. techn. Physik*, 1928, 9, 98.

<sup>2</sup> H. Feuchter, *Kautschuk*, 1926, 2, 260, 282.

<sup>3</sup> G. S. Whitby, *J. Physic. Chem.*, 1932, 36, 198.

1. The elastic recovery at constant temperature.
2. Further recovery on raising the temperature.
3. The non-recoverable extension or plastic flow.
4. The decay of tension at constant extension.

Finally an attempt is made to draw certain inferences from the results of these experiments concerning the structure of raw rubber.

## 2. Experimental Methods.

The rubber used in these experiments was Malayan crepe. Its average molecular weight ( $M$ ) was determined from viscosity measurements in dilute benzene solutions. The ratio of specific viscosity ( $\eta_{sp}$ ) to concentration ( $c$ ), expressed in g. per 100 c.c. solution, extrapolated to infinite dilution was 7.0. Applying Staudinger's equation

$$\frac{k\eta_{sp}}{c} = M$$

and assuming his value <sup>4</sup> of the constant  $k$  for rubber, *i.e.*, 22,000, a figure of 154,000 was obtained for the average molecular weight.

**Preparation of Specimens.**—One difficulty experienced in working with raw rubber is to obtain the material in a form suitable for carrying out mechanical tests. For this purpose it is important that the rubber should be of uniform texture and thickness. In these respects crepe in its commercial form is unsuitable. To overcome this difficulty films were prepared by pouring a 4 % solution of the rubber in benzene on to a flat surface and drying off the solvent. In the first attempts the solution was poured into a frame standing on a glass plate, but films prepared in this way were found to be in a state of internal strain which arose from the inability of the solvent-swollen rubber to contract freely during drying owing to its adhesion to the glass. This was a serious difficulty, for the strain thus introduced could not easily be removed, and it is clearly of the utmost importance in experiments of the kind contemplated that the material worked on shall be strain-free initially. The difficulty was overcome by pouring the solution on to a mercury surface with a confining boundary consisting of a zig-zag paper strip floating edgewise on the mercury, as depicted in Fig. 1. Such a boundary offers no appreciable resistance to the uniform contraction of the film during drying, the contraction actually obtained amounting to 35 % of the linear dimensions. Films prepared by this process were practically strain-free, as judged by the methods to be described later.

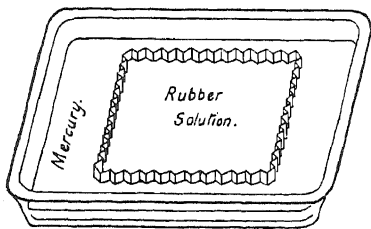


FIG. 1.—Preparation of rubber films from solution.

From the films thus prepared, whose thickness was in the neighbourhood of 0.3 mm., straight test-pieces 40 mm. long and 5 mm. wide were cut. In the experiments a free length of 30 mm. between grips was used, measurements being taken on a marked length of 10 mm. in the middle of the specimen.

**The Stretching Machine.**—The essential details of the stretching machine employed are shown in Fig. 2. The upper grip  $G_1$  was hung by a steel wire from the flat steel spring  $S$  the deflection of which could be read on the scale  $C$ . The lower grip  $G_2$  was connected by a cord passing round pulleys  $P_1$   $P_2$   $P_3$  to the 1 Kg. weight  $W$ . The release of this weight by

<sup>4</sup> H. Staudinger, *Ann.*, 1931, 488, 127; *Ber.*, 1930, 63, 921.

means of the trigger T caused a rapid extension of the test-piece. The supporting rod R was of glass, a material preferred to metal on account of its lower thermal conductivity. The specimen could be surrounded by

a tube A which was immersed in a constant-temperature bath. In no case was liquid used in direct contact with the rubber.

By this arrangement the tension could be observed whilst the specimen was stretched approximately to a constant length. There was, of course, a small change of length due to the movement of the spring; this was not more than 2% of the stretched length of the specimen during any experiment.

In carrying out the experiments the unstretched specimen was inserted in the thermostat, and after a suitable warming-up time the weight was released. Commencing 5 seconds after releasing the weight, readings of tension were taken at suitable intervals throughout the period of extension. At the end of this time the stand was lifted so as to remove the specimen, still stretched, from the thermostat,

and an interval, generally 5 minutes, was allowed for the rubber to cool down below 25° C. The tension was then released, the lower end of the specimen cut off below the marking to remove unnecessary weight, and the specimen transferred to the 25° C. thermostat. Subsequent changes of length were then noted over a 20-hour period.

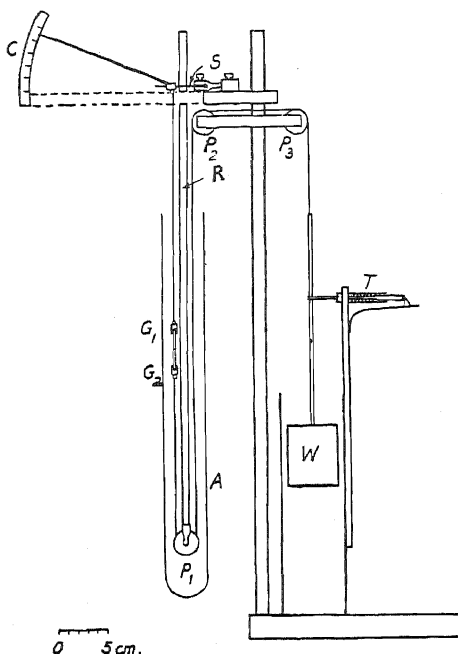


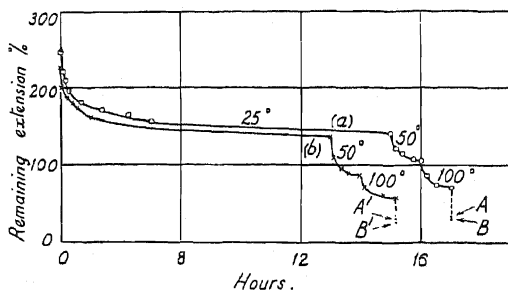
FIG. 2.—The stretching machine.

### 3. The Removal of Strain from Stretched Rubber.

The general nature of the recovery phenomena observed after raw rubber has been stretched are shown in Fig. 3, curve (a), which depicts the

FIG. 3.—Elastic recovery of crepe at temperatures indicated after stretching to 390% extension for 1 hour at 50° C.

- (a) Normal.
- (b) Vacuum treated.



behaviour of a specimen of crepe after stretching at 50° C. for 1 hour at an elongation of 390%. At 25° C. there was an immediate recovery to 260% elongation on releasing the tension. Thereafter there was a further recovery, rapid at first, then progressively slower, over a period of 20 hours. Increas-

ing the temperature to 50° C. caused a sharp increase in the rate of recovery, but with continued heating the rate again slowly diminished. At 100° C. the same phenomenon was repeated. Even then the elastic recovery was not complete. For the further removal of strain two methods were tried, both depending on the swelling action of a solvent. In the first method the specimen was hung in a vessel containing some benzene and the vapour allowed to act on the rubber for a certain time, after which it was removed and dried. The permissible swelling was limited by the tendency of the rubber to sag, so that several successive treatments were usually necessary to secure constancy of length. In the second and preferred method the rubber was immersed in a liquid benzene-alcohol mixture, removed after a suitable time, and dried. This method avoids the sagging difficulty and also permits of a control over the amount of swelling by variation of the benzene content of the mixture. The results obtained by the two methods were in close agreement.

In Fig. 3 the point A represents the remaining extension after treatment for 16 hours by a mixture containing equal volumes of benzene and alcohol. The point B represents a further treatment for the same time by a mixture containing 60 % of benzene. It will be noted that these treatments led to a reduction of the residual extension by more than 50 %. It is hardly possible to use a mixture containing a higher percentage of benzene, owing to the difficulty of handling such highly-swollen rubber. However, since the effect of the 60 % mixture was not very much greater than that of the 50 % mixture, it may be assumed with some confidence that the final length of the rubber represents, if not a complete removal of elastic strain, at least a close approach to that condition. The remaining extension may therefore be regarded as a genuine plastic flow.

**Possible Effects due to Retained Solvent.**—The preparation of specimens from solutions is open to the criticism that there might be a trace of solvent left in the rubber even after several days' drying at room temperature, the presence of which might seriously affect the mechanical properties. To meet this criticism a piece of rubber prepared in the usual way was heated to 50° C. for 8 hours in a high vacuum, with liquid air applied to the evacuated tube, a treatment which should have been sufficient to remove any remaining solvent. The rubber was stretched at 50° C. by means of a falling weight, and the recovery was observed first at 25° C. and then at higher temperatures, both the stretching and recovery being completed without admitting air to the tube. The rubber was then removed and treated with benzene-alcohol mixture in the usual way. The result of this experiment is shown in Fig. 3, curve (b), from which it is clear that the precautions taken made no marked difference either to the amount of the elastic recovery at any temperature or to the plastic flow, and it may therefore be concluded that the results reported are not in error on account of absorbed solvent. At the same time this experiment proves that the possible presence in the rubber of water absorbed from the atmosphere was not having an important effect.

#### 4. The Phenomena of Elastic Recovery.

**Recovery at 25° C. after Stretching at 25° C.**—Fig. 4 shows the recovery curves obtained at 25° C. for samples stretched for 1 hour at 25° C. to various elongations. Noteworthy features of these curves are that for the higher elongations there is no further recovery after the first half-hour, whilst for the lower elongations the recovery is more gradual, and also more complete.

**Recovery at 25° C. after Stretching at 50° C.**—Similar data for samples stretched for 1 hour at 50° C. are given in Fig. 5. It will be observed that the gradualness of the recovery is more noticeable at this stretching temperature than at 25° C., and that the absence of gradual recovery is apparent only after relatively high initial elongations.

**Recovery at Temperatures above 25° C. Crystallisation.**—The recovery curves at 25° C. thus fall into two main classes. In the first the recovery after releasing the tension is relatively small and ceases within about 30 minutes, whilst in the second the recovery is relatively large, and

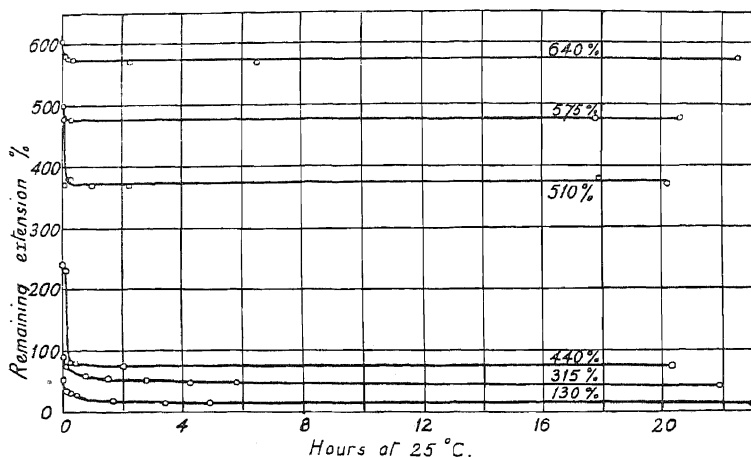


FIG. 4.—Recovery at 25° C. after stretching 1 hour at 25° C. Elongations as marked.

continues at a diminishing rate for at least 20 hours. The high extensions yield recovery curves of the first type, and the low extensions those of the second. Increase of stretching temperature favours the second type.

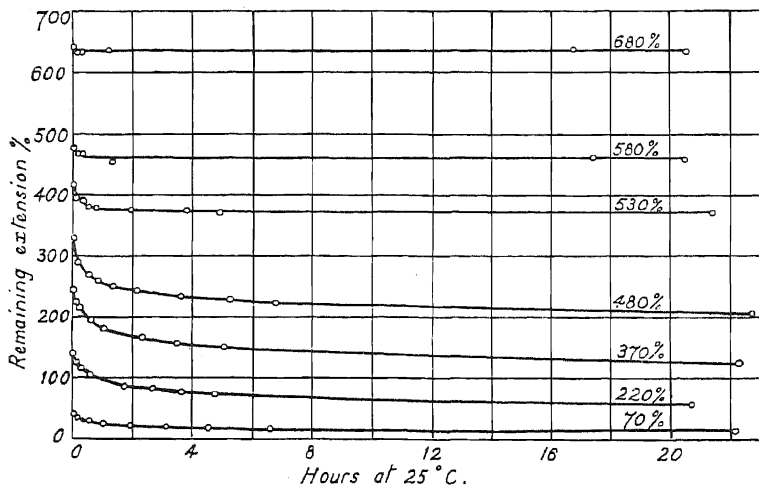


FIG. 5.—Recovery at 25° C. after stretching 1 hour at 50° C. Elongations as marked.

Two types of behaviour are also observed when the recovery at higher temperatures is examined. There is the type of behaviour represented in Fig. 3, in which each increase in temperature gives a slight increase in the recovery; this type of behaviour corresponds with the lower degrees of extension. An entirely different type of behaviour is depicted in Fig. 6, which shows the effect of raising the temperature at the rate of about 1° C. per 3 minutes. The specimens represented in this figure had been extended

at 25° C. for 1 hour and subsequently allowed to recover for 20 hours at 25°. For the higher extensions practically the whole of the subsequent recovery occurred quite quickly over a temperature interval of only 1° C.

Similar experiments on specimens stretched at 50° C. are more interesting because they show clearly the transition between the gradual and the critical-temperature types of recovery (Fig. 7). For the highest extension the temperature range over which most of the recovery occurred was as narrow as for a stretching temperature of 25°, but as the initial elongation was reduced the recovery range showed a corresponding broadening, until for an initial elongation of 480 % all signs of a special recovery temperature had disappeared.

These phenomena have been observed by a number of authors, in greater or less degree, and an explanation of the sharpness of the recovery temperature for highly-extended rubber has been given by Feuchter and Hauser.<sup>5</sup> These workers found that on storing rubber "racked" to 600 %

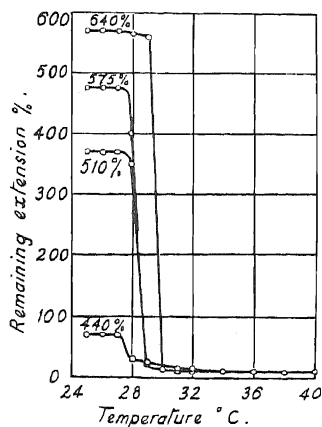


FIG. 6.—Recovery with rising temperature after stretching for 1 hour at 25° C. to extensions indicated.

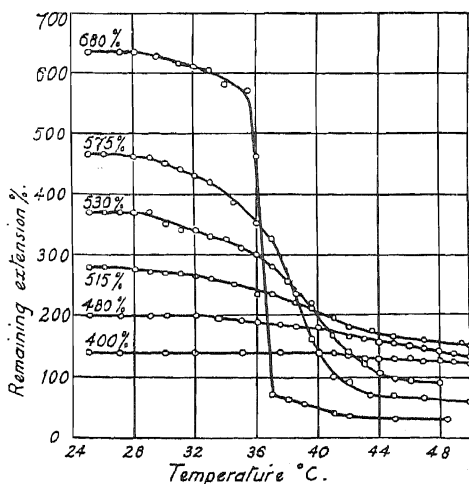


FIG. 7.—Recovery with rising temperature after stretching for 1 hour at 50° C. to extensions indicated.

extension the recovery range narrowed from 11° to 1°, and at the same time there was an increase in density of the rubber and an increase in the intensity of the X-ray "fibre" pattern. They concluded that these phenomena were associated with a high degree of crystallinity. On this view the recovery temperature is to be identified with the melting-point of the crystals formed on stretching.

The data here brought forward generally tend to substantiate this view. It is to be expected, and it has been demonstrated by von Susich<sup>6</sup> from X-ray evidence, that the appearance of crystallisation requires a higher degree of extension the higher the temperature at which the extension is carried out. Hence the critical-temperature type of recovery would be expected to occur more readily at a lower than at a higher temperature, as is indeed found to be the case. There is, however, one feature of the experimental results for which no obvious explanation can be found, namely that the recovery temperature depends on the temperature at which the stretching is performed (cf. Figs. 6 and 7). One would not expect the

<sup>5</sup> H. Feuchter and E. A. Hauser, *Kautschuk*, 1929, 5, 194, 218, 245, 276.

<sup>6</sup> G. von Susich, *Naturwiss.*, 1930, 18, 915.



melting-point of the crystals to depend on the temperature at which they were formed.

### 5. Plastic Flow.

After recovery at 25°, followed in some cases by further recovery at higher temperatures, the samples were treated by a benzene-alcohol mixture containing 50 % of benzene for 16 hours, followed by a further treatment with a 60 % benzene mixture for the same time. The extensions remaining after this treatment, representing plastic flow, are shown in

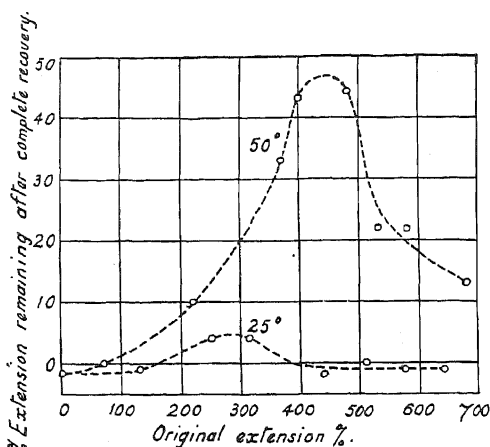


FIG. 8.—Plastic flow expressed as percentage of undeformed length for specimens held for 1 hour at various extensions at the temperatures indicated.

presented were repeated in a number of separate series of experiments. It is desired to draw attention especially to the following points:—

1. The plastic flow increased to a maximum at intermediate extensions, and fell again at higher extensions.
2. The maximum flow on stretching at 25° C. occurred at an elongation of about 300 %, and amounted only to about 2 % of the original extension.
3. For a stretching temperature of 25° the flow was negligibly small for extensions exceeding 400 %.
4. For a higher stretching temperature, *i.e.*, 50° C., the maximum flow occurred at a higher elongation, and the flow at any given elongation was higher.

If we accept the view that the total effect of cohesion between molecules in a crystalline lattice is greater than that between molecules in the disordered state, the reduction of flow which occurred when a certain extension was exceeded may be explained as being due to the occurrence of crystallisation. The fact that the maximum flow occurred at a higher elongation at the higher temperature would appear to be a direct result of the lesser degree of crystallinity at any given elongation. The general features of the flow phenomena are thus explicable on the same basis as the general features of the recovery phenomena dealt with in section 4.

Whitby, from his experiments,<sup>3</sup> drew the conclusion that the amount of flow increased with the elongation. However, he worked only up to 350 % elongation, *i.e.*, on one side only of the maximum in the flow-elongation curve.

### Some Consequences of the Observed Flow Phenomena.

Besides being of interest from the theoretical point of view the peculiar relation between plastic flow and initial elongation leads to certain considerations of practical importance. Since the flow is greatest at intermediate extensions, it is necessary that the intermediate region should be passed through as quickly as possible if the smaller flow characteristic of the higher elongations is to be observed. This is one of the reasons for the adoption, in the present work, of an automatic method of securing rapid extension of the rubber. Moreover, the effect undoubtedly has a bearing on the shape of the stress-strain curves obtained by Rosbaud and Schmid.<sup>1</sup> It accounts also for the observation of Hauser<sup>7</sup> that an X-ray fibre diagram could not be obtained when raw rubber was stretched very slowly, for in this case the region of maximum flow may never have been

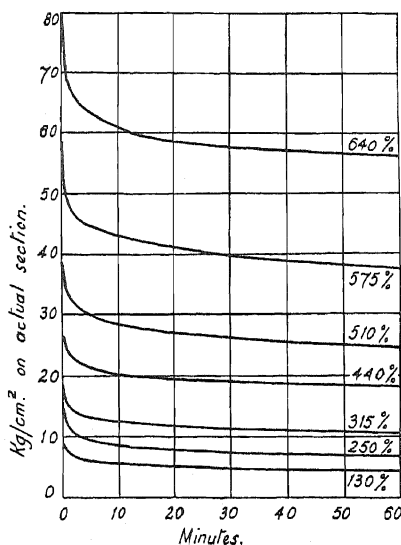


FIG. 9.—Decay of tension at constant extension at 25° C.

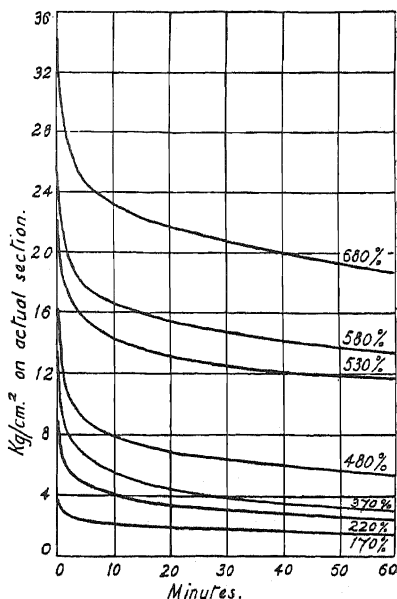


FIG. 10.—Decay of tension at constant extension at 50° C.

passed through and the molecular extension necessary for crystallisation thus not achieved. Finally, it reveals the importance of making a careful study of the accompanying flow before attempting to discuss the meaning of the variations in the shape of stress-strain curves obtained at different temperatures and rates of elongation, and of the hysteresis observed in the stress-strain relationship. These effects are further complicated by the variation of tension with time, even when the flow is negligible. (See below.)

### 6. The Decay of Tension during Extension.

The change of tension with time, for specimens held at constant length, is shown in Figs. 9 and 10. In plotting these curves the observed tensions have been converted to Kg. per cm.<sup>2</sup> referred to the strained cross-section, assuming the density to remain unaltered by the extension. Two features of these curves call for special comment. Firstly, for a given elongation the relative fall of tension is greater at the higher temperature, whilst at

<sup>7</sup> E. A. Hauser, *Kautschuk*, 1927, 3, 288; *Ind. Eng. Chem.*, 1927, 19, 169

a given temperature it diminishes with increasing elongation. Secondly, the tension for a given elongation at  $50^{\circ}$  is in all cases very much lower than for the same elongation at  $25^{\circ}$ . This second result is not consistent with what is deduced from the simplest application of the statistical theory of rubber elasticity developed by Kuhn<sup>8</sup> among others, according to which the tension at constant elongation is directly proportional to the absolute temperature. A linear rate of increase of tension with temperature has indeed been observed by Hauk and Neumann<sup>9</sup> for a number of vulcanised rubbers. The discrepancy cannot be disposed of by taking account of the plastic flow during stretching, this effect being much too small. A difficulty arises also in explaining the fall of tension at a fixed extension. For example, reference to Figs. 8 and 9 shows that a fall of 30 % may occur in the course of 1 hour for rubber elongated by 510 % at  $25^{\circ}$ , though the flow under these conditions is negligible. How, then, is the fall to be explained?

### 7. The Structure of Raw Rubber.

As a basis for the present discussion the statistical theory of the behaviour of single molecules developed by Kuhn<sup>8</sup> will be taken as fundamentally correct. According to this theory the essential elasticity of rubber is a property of the long-chain molecules of which it is composed. The tension exerted by an extended molecule represents the tendency for it to take up the statistically most probable overall length.

In order to account for the elastic properties of a solid, however, it is necessary to consider not only single molecules but also the aggregate of molecules and the forces between them. The molecules in unstretched rubber must be variously intertwined in an irregular manner. The process of extension, by which the molecules become straightened out, at least partially, and orientated in the direction of stretching, must therefore involve considerable relative displacements between adjacent portions of neighbouring molecules, which the cohesive forces between them are not sufficient to prevent. In other words, the molecules can slide over each other with relative freedom. On the other hand, the fact that the flow is negligibly small at temperatures below  $25^{\circ}$  C. proves that there must be present in the rubber a structure which remains unbroken during the deformation. Therefore, in spite of their relative mobility, the molecules of rubber must be held together at a sufficient number of points for this structure to be preserved. The experimental evidence thus leads directly to the following important conclusion:—

*The molecules of rubber are held together at certain points, or over certain regions, so as to form a three-dimensional structure. On deformation at a temperature not exceeding  $25^{\circ}$  C. a sufficient number of these points of linkage or cohesion are maintained for this structure to remain substantially unchanged.*

It is not suggested that the postulation of a structure of this kind to account for the behaviour of elastic bodies is either new or original, but in view of the fact that raw rubber has been commonly regarded as being very imperfectly elastic, it does seem important that the above conclusion should be explicitly stated. By way of comparison, it is of interest to quote the conclusions arrived at by Busse<sup>10</sup> regarding the necessary conditions for the occurrence of high-elasticity in general. These conditions are:— \*

<sup>8</sup> W. Kuhn, *Koll. Z.*, 1936, **76**, 258.

<sup>9</sup> V. Hauk and W. Neumann, *Z. physik. Chem., A*, 1938, **182**, 285.

<sup>10</sup> W. F. Busse, *J. Physic. Chem.*, 1932, **36**, 2862.

\* Cf. also *First Report on Viscosity and Plasticity*, 2nd Edition, p. 98.

1. "The presence of groups of atoms which form strong, somewhat flexible, fibrous units,
2. "weak or uniform cohesive forces around the fibres,
3. "an interlocking of the fibres at a few places along their length to form a 3-dimensional network. This interlocking may occur through chemical combination, by secondary valence forces, or by mechanical entanglement, and
4. "A means of storing up free energy in the fibres during deformation."

**The Nature of the Cohesive Links between Molecules.**—The results brought forward in this paper show that the links between the rubber molecules (*i.e.*, those referred to under Busse's 3rd condition) begin to break down at an appreciable rate at about 50° C. Therefore they cannot be primary chemical bonds. In this respect raw rubber differs from the vulcanised product, in which the bonds between molecules are of high energy. In raw rubber, the links (condition 3) may be due either to van der Waals' forces or to mechanical entanglements. Now we have seen that when fully extended, raw rubber crystallises. In this case the forces holding the molecules in the crystalline lattice are undoubtedly of the van der Waals' type, for there are no others available. Yet, even in this very favourable case, in which the alignment increases the efficacy of the van der Waals' forces between molecules, the crystals are found to break down completely at a temperature in the neighbourhood of 30° C. Such a mechanism cannot therefore *of itself* account for the persistence at higher temperatures of the links (condition 3) between molecules. It is necessary therefore to introduce Busse's suggestion, namely the conception of mechanical entanglements, *in conjunction with van der Waals' forces*, to account for the observed properties. Such entanglement-cohesions would possess a wide range of energies, hence at any stretching temperature some would break very much more quickly than others. Flow would occur when the number remaining unbroken fell below a certain value. There would appear to be a strong *a priori* probability of the formation of relatively stable linkages by mechanical entanglement if the view is accepted that the rubber molecules are very long (length/diameter > 1000), that they are arranged entirely at random with respect to each other but are at the same time densely packed. Under such conditions two or more molecules might very well become twisted together or looped through each other in such a way that on the application of a shearing force a long time would elapse before separation occurred. Or, to put the matter in another way, the entanglements may be regarded as regions possessing an exceptionally high resistance to flow. If a number of such regions were interconnected by extensible (but unbreakable) molecules, the high viscosity characteristic of these regions would be retained as a property of the substance in bulk, whilst at the same time the general mobility of the individual molecules between the points of entanglement would remain.

A mechanism of this kind accounts qualitatively for a number of features of the mechanical behaviour of raw rubber. Considering first the tension, we have to account for (a) a continuous fall of tension at constant length, without plastic flow, and (b) a lower tension after a given time at any extension at the higher temperature. With regard to (a), a fall of tension of the type shown in Fig. 9 is just what would be expected from a series of links representing a wide range of binding energies. The

low-energy links would break quickly, those of higher energy less quickly, and those of still higher energy (*i.e.*, involving considerable entanglement) very slowly or not at all. Consequently, the tension would fall rapidly at first, and thereafter more and more slowly. The same mechanism accounts for (b), for at a higher temperature all the links would break more quickly.\*

Consider now the recovery phenomena. During extension, simultaneously with the breaking of the original entanglement-cohesions between molecules, there will occur a formation of weaker entanglement-cohesions in the deformed state. The greater the degree of mechanical entanglement formed in the stretched condition, the greater will be the energy required to release the strain thus introduced. An increase of temperature will increase the possibility of the formation of new entanglement-cohesions, firstly because of the greater rate of release of the original linkages, and secondly because of the greater thermal agitation of the molecules. On the other hand, the emergence of a crystalline state will tend to reduce the formation of cohesions of the entanglement type.

These considerations lead to a fuller understanding of the recovery phenomena. The new entanglements formed in the stretched condition, though of the same kind as those originally present in the unstretched rubber, will be less complex, and therefore more readily broken down. As with the original linkages, there will be a wide range of cohesional energies, but the average energy will be lower. Hence on releasing the applied tension the force of retraction resident in the individual molecules will cause the breaking down of the new rather than of the original entanglements. There will be a rapid reduction of length corresponding to the breaking of entanglements of low energy, followed by a progressively more and more gradual recovery, corresponding to the release of those of higher energy. An increase of temperature will clearly increase the rate of recovery, without altering its nature.

The theory, of course, accounts for the recovery phenomena only when crystallisation is not present to an important extent, for under these circumstances, as was pointed out above, the behaviour is controlled by van der Waals' forces rather than by entanglement-cohesions.

### Summary.

In considering existing information on the mechanical properties of raw rubber, it is not generally possible to distinguish between the effects of elastic and of plastic deformation. In the experiments described great care was taken to secure the complete removal of elastic strain, after stretching to various extensions at different temperatures. The plastic flow increased to a maximum with increasing elongation and fell again at higher elongations, an effect attributed to the increase of crystallisation with increasing extension. For rubber held extended for one hour at 25° C. the flow was never greater than 2 % of the original extension, whilst for extensions greater than 440 % or less than 130 % it was negligibly small.

Curves showing the decay of tension at constant extension, and the recovery of length after stretching, in conjunction with the observations on plastic flow, are interpreted in terms of a theory proposed by Busse, according to which the rubber molecules are held together at certain points

\* For a discussion of the rôle of molecular entanglement in vulcanised rubber the reader is referred to the work of Long, Singer and Davey. (*Ind. Eng. Chem.*, 1934, 26, 543) on the time lag in the formation of the X-ray fibre pattern on stretching.

by cohesional linkages of low energy, some of which are broken down during stretching.

The author desires to express his indebtedness to Professor E. K. Rideal who provided facilities at the Laboratory of Colloid Science, Cambridge, for carrying out part of this work, and also to Dr. J. K. Roberts of the same laboratory, who was responsible for directing the course of the research and whose advice and criticism have proved invaluable.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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### NUCLEAR GOLD SOLS. III. LOWER LIMIT OF PARTICLE SIZE.

BY A. BAKER AND F. L. USHER.

*Received 12th February, 1940.*

The very few published investigations relating to particle size in nuclear gold sols have been made, with one exception, with sols prepared by reduction with phosphorus in ether (Faraday's method). In the earliest of these Zsigmondy<sup>1</sup> found that the smallest detectable particles contained  $9.7 \times 10^{-20}$  g. of gold, corresponding with a spherical radius<sup>2</sup> just over 1  $\mu$ , a figure substantially confirmed later by Scherrer<sup>3</sup> by X-ray methods. In 1909 Svedberg<sup>4</sup> measured the diffusion coefficient of amiconic particles and arrived at a value for the radius of 0.94 or 2.16  $\mu$ , according to the formula used; but this must be considered a rough approximation, and the figure itself too small, since no account was taken of the osmotic effect of the counter-ions. Reitstötter,<sup>5</sup> in a much fuller study of nuclear sols, examined the effect of varying the conditions of preparation (purification of materials, use of different solvents), and of diluting the initial gold solution. He found that the quantity of gold per particle could be reduced from  $4.9 \times 10^{-19}$  to  $3 \times 10^{-19}$  g. by a twenty-fold dilution of the original solution, which contained  $1.25 \times 10^{-5}$  g. Au per c.c.; the smallest particles obtained in this way had a radius of 1.5  $\mu$ . Thiessen,<sup>6</sup> using potassium thiocyanate as the reducing agent, estimated by an ingenious but inexact method that the smallest nuclei capable of growth had a radius about 1  $\mu$ . The evidence now available can still be summarised appropriately as was done by Zsigmondy and Thiessen:

<sup>1</sup> Zsigmondy, *Z. Elektrochem.*, 1906, **12**, 633.

<sup>2</sup> It should be noted that in the German literature linear dimensions or "diameters" often refer to the length of a cube edge, not to a spherical radius.

<sup>3</sup> Scherrer, *Nachr. K. Ges. Wiss. Göttingen*, 1918, 98 (*Chem. Centr.*, 1919, **1**, 322).

<sup>4</sup> Svedberg, *Z. physikal. Chem.*, 1909, **67**, 105.

<sup>5</sup> Reitstötter, *Kolloid Beih.*, 1917, **9**, 221.

<sup>6</sup> Thiessen, *Z. anorg. Chem.*, 1929, **180**, 110.

"Up to now gold particles with linear dimensions less than  $1.5 \text{ m}\mu$  have not with certainty been shown to exist, and it is questionable whether particles of metal with fewer than about 300 gold atoms are capable of existence and can form part of a very homogeneous gold sol. . . . We must assume that in the production of gold hydrosols the region that lies between simple gold molecules and aggregates with more than about 300 gold atoms is skipped over rapidly. Particles of intermediate size are not known." <sup>7</sup>

The smallest detectable nuclei, whatever their size, are built up from gold atoms liberated in the chemical reaction, and it is hardly conceivable that this process should take place by encounters of about 300 atoms simultaneously. The alternatives are to assume (1) that the particles are built up atom by atom, or (2) that they are built up by a process analogous to coagulation. In the former event particles of all possible degrees of complexity, and in the latter of a considerable number, must have a transient existence in the region referred to by Zsigmondy. Failure to detect such particles can be easily understood when it is remembered that the magnitude of the stabilising charge increases with the size of the particles, and may be considered, to a first approximation, proportional to their surfaces. There must therefore be a critical size, depending on the experimental conditions, at which the adsorbed ionogenic layer just suffices to confer permanent stability. Particles of smaller size will grow, either by the acquisition of gold atoms or by coagulation with other particles, until the critical size is reached or exceeded. If this view is correct the critical size, and consequently the size of the smallest stable particles, should be influenced by (a) introducing into the reaction mixture ions which might be expected to promote stabilisation, and (b) diluting the reaction mixture so as to reduce the total amount of electrolyte present. Experiments dealing with these two points will now be described.

### Influence of Added Ions.

The ions used were aurocyanide and iodide. The first is relatively stable and should be readily adsorbable on gold because of its chemical structure, whilst iodide has been shown to increase the stability of ordinary gold sols towards electrolytes.<sup>8</sup>

**Effect of Aurocyanide.**— $\text{NaAu}(\text{CN})_2$  was made by digesting excess of freshly precipitated  $\text{AuCN}$  with a solution of  $\text{NaCN}$ . A slightly alkaline solution of  $\text{KAuCl}_4$  was divided into three parts, one of which (A) was made  $0.007 \text{ M.}$ , and another (B)  $0.0007 \text{ M.}$  with respect to  $\text{NaAu}(\text{CN})_2$ , whilst the third (C) contained none. All three were then reduced with phosphine under otherwise identical conditions, the resulting nuclear sols containing  $10^{-5} \text{ g. Au per c.c.}$  The size of the nuclei was determined in each of the three sols by the method described in Part I.<sup>9</sup> The results were: Sol A,  $r = 1.49, 1.54, 1.64, 1.68$ , mean  $1.6 \text{ m}\mu$ ; sol B,  $r = 1.81, 1.79, 1.86, 1.90, 1.80$ , mean  $1.85 \text{ m}\mu$ ; sol C,  $r = 1.66, 1.52, 1.65$ , mean  $1.6 \text{ m}\mu$ . Thus the particle size was not smaller in the presence of aurocyanide. The sols A and B began to turn purple after several days and showed signs of sedimentation after a month, whilst C remained quite stable. It is evident that aurocyanide lessens the stability of gold sols.

<sup>7</sup> Zsigmondy and Thiessen, *Das kolloide Gold*, Leipzig, 1925, 84.

<sup>8</sup> Krut and Nierstrasz, *Kolloid Z.*, 1937, 78, 26.

<sup>9</sup> Usher, *Trans. Faraday Soc.*, 1938, 34, 1230.

**Effect of Iodide.**—Three solutions of  $\text{KAuCl}_4$ , each containing  $10^{-5}$  g. Au per c.c., were made 0,  $2 \times 10^{-5}$ , and  $2 \times 10^{-4}$  M. with respect to KI, and reduced with phosphine. After standing overnight the sols containing iodide were still yellow, whilst the other had turned pink. On boiling, all three were red. The respective particle sizes were 2.8, 3.0, and 4.8  $\mu$ . It is thus clear that the size is slightly increased by the presence of potassium iodide. The sols with iodide became purple after a month but showed no sign of sedimentation.

An attempt was made to determine the effect of aurate ions, but the aurate was found to be reduced by phosphine to an extent depending on the  $\text{pH}$  of the solution, and no trustworthy inference could be drawn. In no experiment was any decrease of size found.

### Influence of Dilution.

Reitstötter's experiments<sup>5</sup> were made with solutions containing  $1.25 \times 10^{-5}$  g. Au per c.c. which were diluted in four stages to a final concentration of  $6.25 \times 10^{-7}$  g. per c.c., whilst the amount of phosphorus used for reduction was kept constant. It was argued that if reduction took place at the surface of the colloidal phosphorus particles the mass of the individual gold nuclei would decrease proportionally with dilution, since the number of reducing centres would remain approximately the same. The actual effect of the dilution, however, was to reduce the number of nuclei from  $2.6 \times 10^{13}$  to  $2.1 \times 10^{13}$  per c.c., corresponding with a decrease in radius from 1.8 to 1.5  $\mu$ . This decrease of size, corresponding with a difference of 60 per cent. in the quantities actually measured (*i.e.* the number of particles derived from a given weight of gold), is well beyond the limits of experimental error and must be considered real. Its significance consists in showing that dilution is one means by which the size of gold nuclei can be diminished; no other has yet been discovered. The twenty-fold range of concentration studied by Reitstötter enabled him to prove that no obvious relation existed between the number of phosphorus particles and the number of gold nuclei, but to gain a satisfactory insight into the relation between concentration and particle size it is clearly desirable to extend the range considerably. The experiments described below were made with this object.

Two series of measurements were made, the nuclear sols being prepared by the phosphine method<sup>10</sup> in the first and by the hydrogen sulphide method<sup>10</sup> in the second. The sols were made by adding the phosphine or hydrogen sulphide solution to 30 c.c. of a solution of  $\text{KAuCl}_4$ , suitably diluted, and slightly alkaline in the first case but neutral in the second; the final volume was always 50 c.c. In every case the sols were boiled for 5 minutes and air was bubbled through them for 30 minutes to remove the excess of the reducing agent ( $\text{PH}_3$  or  $\text{H}_2\text{S}$ ). The range of concentration studied was  $2 \times 10^{-4}$  to  $2 \times 10^{-9}$  g. Au per c.c. in the phosphine series and  $8 \times 10^{-4}$  to  $2 \times 10^{-9}$  g. per c.c. in the hydrogen sulphide series. For the size determinations a solution of  $\text{KAuCl}_4$  containing 1 mg. of gold was mixed with such a quantity of the diluted nuclear sol as would furnish particles in the size range corresponding with a purple colour, and the colour of the resulting sol was matched in the way described in Part I.<sup>9</sup> To ensure even growth and to reduce the chance of fresh nuclei being formed during reduction, the hydroxylamine (12.5 c.c. of a solution containing 0.27 g.  $\text{NH}_2\text{OH}$ ,  $\text{HCl}$  per litre) was added very slowly from a Jena glass burette with ungreased stopcock at the rate of 1 drop every 5 seconds for the first half and at twice this rate for the second half of the reduction.

<sup>10</sup> Baker and Usher, *Trans. Faraday Soc.*, 1940, **36**, 385.



The mixture undergoing reduction was contained in a 100 c.c. Pyrex flask clamped to a tilted base which was mechanically shaken while the mouth of the flask remained stationary under the burette. Since the colour of the grown sols is determined only by the particle size the number of particles is obtained by a simple calculation, and if this number can be assumed to be the same as that of the nuclei in the added nuclear sol the size of the particles in the latter can be calculated from the known weight of gold contained in it. If, however, the operations involved in growing the sols cause the formation of any fresh nuclei, the number ultimately found will be too large, and the calculated size too small. It is therefore necessary first to determine the magnitude of the correction to be applied if this source of error is present.

**Formation of Fresh Nuclei During Reduction.**—Although hydroxylamine is a reducing agent of the "non-nuclear" type, nuclei are in fact produced when it is mixed with a gold solution to which no ready-formed nuclei have been added. Westgren<sup>11</sup> showed that if the concentration of ready-formed nuclei in the reaction mixture falls below about  $2 \times 10^{10}$  per c.c. some fresh nuclei are formed when hydrogen peroxide is used as the reducing agent, but that if this concentration is exceeded all the gold formed in the reaction is deposited on the nuclei already present and the total number of particles remains the same. Hydroxylamine has a smaller tendency than hydrogen peroxide to produce nuclei, but no figures are available for it. However, it is possible to fix an upper limit from the data for one of the sols made in the course of calibrating the colour standard used in this investigation. This sol was made by reducing 1 mg. of gold as  $\text{KAuCl}_4$  in the presence of a small quantity of nuclear sol, and the resulting particles were found from the rate of sedimentation to have a radius of  $84 \text{ m}\mu$ . This size corresponds with  $2 \times 10^{10}$  particles, the volume of the sol being 40-50 c.c. Since the calculated number of particles in the original nuclear sol agreed with that obtained from other similar experiments in which a larger proportion of nuclear sol was used, it is certain that no extraneous nuclei were present, and it can therefore be safely assumed that the concentration of nuclei produced by hydroxylamine under these particular conditions does not exceed  $5 \times 10^8$  per c.c., and is probably smaller. The correction to be applied on this account in any of the determinations given below is smaller than the experimental error. A further possibility has now to be considered. The reducing agents used in the preparation of the nuclear sols, *viz.*, phosphine and hydrogen sulphide, are specially active in promoting the formation of nuclei, and any trace of them remaining in the nuclear sol will cause some fresh nuclei to be formed as soon as the gold solution used for growing the particles is added. The procedure regularly adopted to remove the gases from solution, *viz.*, to boil the liquid for 5 minutes and then to pass air through them for half an hour, cannot be expected to be completely effective, and it was therefore necessary to carry out blank experiments in which particles were grown by the standard method in the presence of measured quantities of a "nuclear sol" which had been treated exactly as described above, but which contained no gold. When this was done, fresh nuclei were formed in numbers nearly proportional to the amount of blank "nuclear sol" used, and these numbers were used as corrections to those found when real nuclear sols were substituted for the blank one. The results are in Table I.

There are thus two sources of unwanted nuclei: one is the conductivity water and other reagents, which are responsible for about  $2 \times 10^{10}$  with the quantities used in these experiments, and the other is the residual traces of reducing gas present in the nuclear sols, which give rise to  $4.7 \times 10^{11}$  and  $2.8 \times 10^{11}$  per c.c. of the phosphine and sulphide sols respectively; these make up the total (*i.e.*, the number actually determined)

<sup>11</sup> Westgren, *Z. anorg. Chem.*, 1915, 93, 156.

shown in the third column of Table I. In experiments made to determine the amount of gold ( $w_n$ ) in each particle of a particular nuclear sol the corrected value is then  $w_n = cvw_g / (10^{-3} - kvw_g)$ , where  $w_g$  is the experimentally determined weight of each particle in the grown sol,  $c$  is the concentration (g. per c.c.) of gold in the nuclear sol,  $v$  the (undiluted) volume of the latter, and  $k$  the number of extra nuclei produced by 1 c.c. of nuclear sol, as derived from the data in Table I; the  $10^{-3}$  represents the total weight, 1 mg., of gold used in every case. The correction thus introduced is a maximum correction, since it implies that all the extra nuclei found when a blank "nuclear sol" is used are also formed in the presence of added nuclei. The results are shown in Table II to two significant figures.

It has been shown<sup>10</sup> that gold sulphide nuclei, which are present in the nuclear sols used in the second series of measurements, form effective condensation centres for metallic gold. The particles grown on these nuclei contained from 2000 to 2,000,000 times as much gold as the nuclei

TABLE I.

Reducing Agent.	Blank Nuclear Sol. (c.c.).	Radius of Particles from 1 mg. Au $\mu\mu$ .	Total No. of Particles formed ( $\times 10^{11}$ ).	No. of Particles per c.c. of Blank Sol ( $\times 10^{11}$ ).
Phosphine . .	1.0	29	5.02	5.0
" . .	0.5	37	2.41	4.8
" . .	0.33	40.5	1.84	5.5
				Mean . 5.1
Hydrogen sulphide	2.0	28	5.59	2.8
" "	1.5	30.5	4.31	2.9
" "	1.0	34.5	2.98	3.0
" "	0.67	38.5	2.14	3.2
				Mean . 3.0

themselves, and were of course indistinguishable from particles grown on metallic nuclei. The results in this series are less regular than those in the first, but are otherwise similar. The obvious misfits ( $N_7$ ,  $N_{15}$ ,  $N_{26}$  and  $N_{28}$ ) are not due to any error of measurement; they are probably to be attributed to accidental variations in the rate of mixing the reacting solutions, or in the concentration of the solution of reducing agent used in making the sols.

After making allowance for these irregularities and for experimental errors, the figures leave no doubt that the particle size decreases with dilution of the reacting solutions down to an apparent limit where the number of atoms per particle is approximately the same as the number constituting a unit cell of crystalline gold. No useful purpose would be served in carrying the dilution still further, since the correction would then become considerably larger than the quantity being measured and the results would have little value.

### The Formation and Stability of Nuclei.

The distinction generally recognised between the formation of nuclei and their subsequent growth to larger particles is justified on practical grounds, since these two phases of the formation of a colloidal particle are often affected in different ways by a particular set of conditions. This distinction, as well as the use of the terms "nuclei" and "primary particles" with reference either to aerosols or to hydrosols, unfortunately tends to obscure the essential unity of the processes by which particles

of any size are evolved from their parent atoms or molecules. These processes are collision and the mutual adhesion of the units that have collided. In an unstable system such as an aerosol the whole process of building up large particles from molecules is continuous, and must be

TABLE II.

Designation and Concn. of Nuclear Sol (g. Au per c.c.).	Wt. of Nuclei Uncorr. (g. $\times 10^{21}$ ).	Wt. of Nuclei Corr. (g. $\times 10^{21}$ ).	No. of Au Atoms per Nucleus.	Designation and Concn. of Nuclear Sol (g. Au per c.c.).	Wt. of Nuclei Uncorr. (g. $\times 10^{11}$ ).	Wt. of Nuclei Corr. (g. $\times 10^{11}$ ).	No. of Au Atoms per Nucleus.
<b>Sols made with Phosphine:</b>							
			Mean.				Mean.
N12	5400	5400	17000	N16	30	33	100
$2 \times 10^{-4}$	6200	6300	19000	$2 \times 10^{-7}$	38	42	130
	6700	6800	21000		37	41	130
	6000	6100	19000		40	45	140
N13	1100	1100	3500	N17	27	31	96
$8 \times 10^{-5}$	1000	1000	3100	$10^{-7}$	34	41	130
	1000	1000	3100		40	50	150
	1000	1000	3000		39	49	150
N7	1900	2100	6300	N18	17	20	63
$10^{-5}$	1800	2000	6000	$5 \times 10^{-8}$	16	19	60
	1600	1800	5400		15	18	54
	1600	1800	5400		13	15	46
N2	690	750	2300	N19	9.0	11.7	36
$4.1 \times 10^{-6}$	670	730	2200	$2 \times 10^{-8}$	7.6	9.3	29
	650	710	2200		7.2	8.7	27
	450 *	480 *	1500 *		8.3	10.4	32
N14	660	720	2200	N20	3.0	4.9	15
$10^{-6}$	180	200	610	$4 \times 10^{-9}$	3.1	5.0	16
	180	200	600		3.2	5.3	16
	140	150	470		2.7	4.2	13
N15	140	160	500	N21	2.3	5.7	17
$5 \times 10^{-7}$	170	210	650	$2 \times 10^{-9}$	2.0	4.3	13
	190	230	700		2.1	4.5	14
	180	220	680		2.2	5.2	16
<b>Sols made with Hydrogen Sulphide:</b>							
N24	700	710	2200	N29	47	66	200
$2 \times 10^{-5}$	720	730	2300	$5 \times 10^{-8}$	56	84	260
	660	670	2100		60	93	280
	600	600	1900		49	68	210
	630	630	2000	N30	45	79	240
	610	620	1900	$2 \times 10^{-8}$	37	85	260
N25	420	430	1300		37	81	250
$10^{-5}$	410	410	1300		35	73	230
	390	400	1200	N31	13	22	69
	380	390	1200	$10^{-8}$	16	29	88
N26	530	550	1700		20	49	150
$4 \times 10^{-6}$	520	540	1700		18	40	120
	470	480	1500	N32	6.0	11	33
	440	460	1400	$4 \times 10^{-9}$	6.8	14	43
	140	150	470		6.1	11	35
N27	140	150	460		5.5	9.4	29
$8 \times 10^{-7}$	150	160	480	N33	2.3	3.4	11
	160	170	520	$2 \times 10^{-9}$	2.1	3.1	9
	34	36	110		2.1	3.2	10
N28	29	30	92		2.4	3.9	12
$2 \times 10^{-7}$	30	31	96				10

\* Rejected.

presumed to conform in all its stages to purely kinetic principles. The same is true of a stable hydrosol as far as the production of the smallest stable particles—the so-called nuclei; beyond this point collisions are not followed by adhesion, owing to the electric charge which is acquired when a certain degree of complexity has been reached. The stabilising charge is generally understood to be due to either autogenous or adsorbed ions, and Pauli and others<sup>12</sup> have shown that in the case of gold the stabilising ion is probably  $\text{AuCl}_2'$  or  $\text{Au}(\text{OH})\text{Cl}'$ , presumably formed by the partial reduction of the original gold compound. Unfortunately the effect of varying the concentration of this ion in the reaction mixture cannot be studied, since there is no known way of controlling the amount produced. Attempts such as are recorded in this paper to impart a heavier charge, or to impart a charge at an earlier stage of growth, by the addition of other ions which might be expected to be effective, have led to diminished rather than improved stability, as shown by the increased size of the particles. It seems probable either that the stabilising ion that happens to be formed in the reaction is specially effective, or that the sols themselves are unusually sensitive to very small concentrations of electrolyte even when the latter contains an adsorbable anion.

The data presented in Table II show that the size of the smallest stable particles is greatly affected by the concentration of the solution undergoing reduction; the mass of the resulting nuclei is very roughly proportional to the square root of the gold concentration in both the sulphide and the phosphine series. The figures given for the size of the smallest nuclei are subject to an error perhaps as large as 40 per cent. on account of the relatively large correction involved, but it still remains evident that particles of about the size of a unit cell, *i.e.* 14 atoms, can exist and can be detected in a stable sol.

A survey of the course of events leading to the formation of nuclei indicates that the influence of dilution on particle size cannot be explained on purely kinetic grounds. The addition of the reducing agent causes a sudden appearance of gold atoms at a certain concentration  $n_0$ , and these atoms will at once begin to form aggregates by a process analogous to ordinary coagulation. If no stabilising factor is present the particle size will continue to increase indefinitely, but if, as is here assumed, the particles after reaching a certain degree of complexity begin to adsorb stabilising ions, the process must slow down when that stage is reached, and must eventually come to a stop when stabilisation is complete, when no fruitful collisions will occur. It is clear that the influence of  $n_0$  will be strictly confined to determining the frequency of collisions, and that the effectiveness of these must depend on other factors. The observed effect of dilution must therefore be due to some factor other than the mere decrease in the initial concentration of gold atoms, and an explanation of it may be found in the parallel decrease in the concentration of electrolytes. Thiessen<sup>13</sup> showed that the stability of gold sols towards electrolytes increases as the size of the particles decreases over the range 70–20  $m\mu$ ; but it is also known that the stability vanishes altogether at a still lower size; there must therefore be some intermediate size for which the stability is a maximum. Hence in the early stages of growth before this maximum is reached the same degree of

<sup>12</sup> Eirich and Pauli, *Kolloid Beih.*, 1930, 30, 113; Pauli, Russer, and Brunner, *Kolloid Z.*, 1925, 72, 26.

<sup>13</sup> Thiessen, Thater, and Kandelaky, *Z. anorg. Chem.*, 1929, 180, 11.

stability will be attained by a particle in the presence of a certain concentration of foreign electrolyte as is possessed by a smaller particle in the presence of a smaller concentration. These considerations offer a simple and adequate explanation of the experimental results, if it can be assumed that the stability of gold sols really decreases with increasing concentration of electrolyte at the very small concentrations prevailing during their preparation. Evidence for this is to be found in Zsigmondy and Thiessen's statement<sup>14</sup> that gold sols may be concentrated by evaporation to a maximum of about 0.1 per cent., but only if the evaporation is accompanied by dialysis. The more efficient methods of electro-dialysis and electrodecantation have recently enabled Pauli and others<sup>15</sup> to achieve still higher concentrations, up to 5 per cent. Thus it is clear that the stability of gold sols is increased by the removal of electrolyte up to the extreme limits made possible by modern technique. Another possible factor, which may be important at very low concentrations, is the relative quantity of the stabilising ion formed during reduction. Nothing is known as to how this varies with the experimental conditions, but it should be kept in view as a factor the effectiveness of which may vary with the dilution of the gold compound as such, independently of that of the accompanying electrolyte.

The question how far the results obtained with gold may be expected to hold for other substances can be answered only in general terms. It is characteristic of colloidal solutions of gold and other noble metals that their stability increases with the progressive removal of electrolytes, and it is for this reason that in them the smallest particles are formed in sols made from the most dilute solutions. On the other hand substances whose colloidal solutions become unstable or less stable under prolonged dialysis would form the smallest particles at some intermediate dilution. It is clear that each sol must be considered by itself in the light of information about the effect of dilution of the reacting solutions on its stability, an effect which may be due to alteration of the quantity or the composition of the stabilising ion, as well as to the removal of non-stabilising or "foreign" electrolytes.

### Homogeneity and Stability of Nuclear Sols.

With reference to the preparation of unidisperse gold sols it is often tacitly assumed that the nuclear sol used for this purpose is itself unidisperse. This assumption is unfounded. Only if the nuclei were formed by the building up of aggregates atom by atom would the process stop when all the aggregates were of approximately equal size. Such a process is hardly conceivable, since the proportion of single atoms becomes very small at an early stage, and further growth must therefore occur chiefly by the union of aggregates; the inevitable result of this is the formation of more complex aggregates whose sizes will be distributed over a considerable range. There can be little doubt that the size distribution in a nuclear sol, though possibly less symmetrical, is otherwise similar to that found in an ordinary sol made without any special precautions. This inference has a practical bearing on the preparation of unidisperse sols, for if the size distribution curves of nuclear sols with different average sizes are of similar shape, it is clearly advantageous to grow a sol on nuclei of the smallest possible average size, since it is

<sup>14</sup> Zsigmondy and Thiessen, *op. cit.*, 47.

<sup>15</sup> Pauli, Szper and Szper, *Trans. Faraday Soc.*, 1939, **35**, 1178.

the absolute and not the percentage variation in linear dimensions that is reproduced in the grown particles; and for similar distributions the absolute variation will be proportional to the average size.

A further consequence of the suggested mode of evolution of a nuclear sol is that the freshly prepared sol will be only just stable and will therefore be very sensitive to small additions of electrolyte. For a similar reason slight variation in the conditions prevailing while the sol is being prepared may (for example by altering the amount of stabilising agent formed) cause a marked change in the average particle size. This is perhaps the chief cause of the few irregularities appearing in the results quoted in Table II. It has been found on several occasions that the particle concentration of an undiluted nuclear sol has decreased after the lapse of a few months, presumably because even with the strictest precautions some increase in electrolyte content occurs during storage in glass vessels. Changes of this kind can be avoided by diluting the sol with conductivity water immediately after preparation.

### Summary.

1. Previous work on the minimum size of gold nuclei is reviewed.
2. Attempts to reduce the size of nuclei by the addition of adsorbable anions were unsuccessful.
3. Progressive dilution of the reacting solutions over an extensive range resulted in the production of stable nuclei of less than one-tenth the size of the smallest hitherto believed to exist. These nuclei are of approximately the size of a unit cell of crystalline gold.
4. The experimental results are in agreement with the view that the formation of colloidal particles from atoms or molecules is a continuous process governed by the same kinetic principles as are used to explain coagulation. The terms "nuclei" and "primary particles" have no significance apart from their use to describe the smallest particles that are stable or detectable under existing conditions.

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## VISCOSITY OF ELECTROLYTIC MIXTURES IN DILUTE SOLUTION.

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The study of the viscosity of simple electrolytic solutions has received much attention since Jones and Dole<sup>1</sup> proposed their equation  $\eta/\eta_0 = 1 + A\sqrt{c} + Bc$  and Falkenhagen, Dole and Vernon<sup>2</sup> gave a theoretical interpretation of "A" in terms of the interionic attraction theory, and found out a mathematical expression for it involving dielectric constant and viscosity of solvent and the mobility and electric charges of the ions. The problem of solutions containing more than

<sup>1</sup> Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

<sup>2</sup> Falkenhagen and Dole, *Z. physik. Chem. B* 1929, **6**, 159; *Physik. Z.*, 1929, **30**, 611; Falkenhagen and Vernon, *Phil. Mag.*, 1932, **14**, 537.

two species of ions with respect to viscosity has not been studied experimentally as yet in the light of the interionic attraction theory. Such works as those of Stearn,<sup>3</sup> Yajnik and Uberoy,<sup>4</sup> Ruby and Kawai,<sup>5</sup> Tollert,<sup>6</sup> Banchetti<sup>7</sup> and Ishikawa<sup>8</sup> are concerned with either the study of complex salt formation or the application of one or the other of the various mixture law formulæ to the viscosity of mixed electrolytes in solution. Onsager and Fuoss<sup>9</sup> are the only workers who have tackled the problem from a theoretical standpoint, but their treatment is so highly mathematical that their analysis has not been able to stimulate the interest the subject deserves. The net result of their analysis is that in the case of mixtures of electrolytes also "the electrostatic contribution to viscosity is proportional to the square root of concentration."

The idea underlying the present investigation was to examine how a mixture of two electrolytes (with a common ion) in a definite proportion behaved with respect to viscosity when the concentration was changed without affecting the proportion of the components of the mixture by diluting with water and whether the variation in viscosity could be represented by an equation of the Jones and Dole type. The salt pairs examined were (a) sodium chloride and barium chloride, and (b) sodium chloride and magnesium chloride. In each case a number of mixtures containing the two salts in different proportions were examined.

### Experimental.

The experimental technique and procedure have been described in previous communications.<sup>10, 11</sup> The viscometer used had a capillary of 10 cm. length and 0.028 cm. diameter with an upper bulb of 5 c.c. capacity. The approximate time of efflux of water was 29 minutes. No kinetic or surface tension correction was considered necessary. Three readings for the time of flow were taken with a Venner time switch graduated in tenths of seconds, agreeing with one another within 0.2 sec. The time for water was determined before and after each solution. The pycnometer was one of about 64 c.c. capacity. The density figures are the results of two determinations, differing by less than 1 mg., the weights being reduced to vacuum standard.<sup>12</sup> Double distilled water was used in all the experiments. The thermostat was maintained at  $35^\circ \pm 0.005^\circ \text{C}$ . The error in viscosity measurements is expected to be less than three parts in ten thousand and densities are accurate to sixteen parts in a million.

Merck's *pro-analysi*  $\text{BaCl}_2$ , reagent quality  $\text{MgCl}_2$  and *pro-analysi*  $\text{NaCl}$  were used. Standard solutions of these salts were prepared and their strengths were determined. Barium chloride was estimated gravimetrically as  $\text{BaSO}_4$ ,  $\text{MgCl}_2$  as  $\text{AgCl}$  after eliminating  $\text{Mg}$  by precipitation as  $\text{MgCO}_3$ , and  $\text{NaCl}$  by direct weighing after drying in an air oven at  $130^\circ \text{C}$ . Mixtures having the two salts in different proportions were prepared by mixing the solutions in proper proportion. The mixtures were then diluted to decrease their concentration to the required level.

The results are tabulated below. Total concentrations are given in gram moles per litre and densities are expressed in grams per c.c.  $\eta/\eta_0(\text{obs.})$

<sup>3</sup> Stearn, *J. Amer. Chem. Soc.*, 1922, 44, 670.

<sup>4</sup> Yajnik and Uberoy, *ibid.*, 1924, 46, 802.

<sup>5</sup> Ruby and Kawai, *ibid.*, 1926, 48, 1120.

<sup>6</sup> Tollert, *Z. physik. Chem., A*, 1935, 172, 129.

<sup>7</sup> Banchetti, *Gazz. Chim. Ital.*, 1934, 64, 229; 1935, 65, 159; 1936, 66, 446.

<sup>8</sup> Ishikawa, *Bull. Chem. Soc. Japan*, 1937, 12(1), 16.

<sup>9</sup> Onsager and Fuoss, *J. Physic. Chem.*, 1932, 36, 2689.

<sup>10</sup> Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, 34, 1139.

<sup>11</sup> Chacravarti and Prasad, *ibid.*, 1939, 35, 1466.

<sup>12</sup> Srinivasan and Prasad, *ibid.*, 1462.

and  $\eta/\eta_0$  (calc.) are the relative viscosities, observed and calculated from the equation. The divergence ( $\Delta$ ) between the two is given in the last column.

TABLE I.

Total Concentration.	Density.	$\eta/\eta_0$ (obs.).	$\eta/\eta_0$ (calc.).	$\Delta \times 10^4$	Total Concentration.	Density.	$\eta/\eta_0$ (obs.).	$\eta/\eta_0$ (calc.).	$\Delta \times 10^4$
Pure NaCl; $\eta/\eta_0 = 1 + 0.006\sqrt{c} + 0.102c$ .					[NaCl]/[MgCl <sub>2</sub> ] = 4; $\eta/\eta_0 = 1 + 0.009\sqrt{c} + 0.165c$ .				
0.0100	0.994478	1.0016	1.0016	0	0.0100	0.994547	1.0027	1.0026	+1
0.0200	0.994870	1.0030	1.0028	+2	0.0200	0.995020	1.0046	1.0046	0
0.0300	0.995255	1.0041	1.0041	0	0.0300	0.995518	1.0067	1.0066	+1
0.0400	0.995669	1.0053	1.0053	0	0.0400	0.995999	1.0083	1.0084	-1
0.0500	0.996076	1.0065	1.0064	+1	0.0500	0.996499	1.0102	1.0103	-1
0.0600	0.996467	1.0076	1.0076	0	0.0600	0.996982	1.0122	1.0121	+1
0.0700	0.996872	1.0087	1.0087	0	0.0700	0.997468	1.0140	1.0140	0
[NaCl]/[BaCl <sub>2</sub> ] = 3; $\eta/\eta_0 = 1 + 0.009\sqrt{c} + 0.132c$ .					[NaCl]/[MgCl <sub>2</sub> ] = 3/2; $\eta/\eta_0 = 1 + 0.011\sqrt{c} + 0.220c$ .				
0.0100	0.994771	1.0020	1.0022	-2	0.0100	0.994624	1.0034	1.0033	-1
0.0200	0.995111	1.0039	1.0039	0	0.0200	0.995181	1.0059	1.0060	-1
0.0300	0.996270	1.0056	1.0056	0	0.0300	0.995762	1.0083	1.0085	-2
0.0400	0.997033	1.0074	1.0071	+3	0.0400	0.996306	1.0109	1.0110	-1
0.0500	0.997767	1.0086	1.0086	0	0.0500	0.996880	1.0134	1.0135	-1
0.0600	0.998508	1.0101	1.0101	0	0.0600	0.997429	1.0160	1.0159	+1
0.0700	0.999257	1.0115	1.0116	-1	0.0700	0.997998	1.0182	1.0183	-1
[NaCl]/[BaCl <sub>2</sub> ] = 1; $\eta/\eta_0 = 1 + 0.011\sqrt{c} + 0.170c$ .					[NaCl]/[MgCl <sub>2</sub> ] = 2/3; $\eta/\eta_0 = 1 + 0.013\sqrt{c} + 0.282c$ .				
0.0100	0.995136	1.0026	1.0028	-2	0.0100	0.994690	1.0042	1.0041	+1
0.0200	0.996235	1.0048	1.0050	-2	0.0200	0.995327	1.0077	1.0074	+3
0.0300	0.997344	1.0069	1.0070	-1	0.0300	0.995963	1.0107	1.0107	0
0.0400	0.998421	1.0090	1.0090	0	0.0400	0.996605	1.0138	1.0139	-1
0.0500	0.999519	1.0112	1.0110	+2	0.0500	0.997248	1.0167	1.0170	-3
0.0600	1.000595	1.0129	1.0129	0	0.0600	0.997930	1.0198	1.0201	-3
0.0700	1.001687	1.0150	1.0148	+2	0.0700	0.998582	1.0230	1.0231	-1
[NaCl]/[BaCl <sub>2</sub> ] = 1/3; $\eta/\eta_0 = 1 + 0.015\sqrt{c} + 0.205c$ .									
0.0100	0.995479	1.0034	1.0036	-2					
0.0200	0.996866	1.0062	1.0062	0					
0.0300	0.998319	1.0086	1.0088	-2					
0.0400	0.999720	1.0114	1.0112	+2					
0.0500	1.001152	1.0137	1.0137	0					
0.0600	1.002580	1.0159	1.0160	-1					
0.0700	1.003987	1.0183	1.0184	-1					

### Discussion.

The applicability or otherwise of the Jones and Dole equation in case of any mixture having the two salts in a fixed proportion was tested by plotting  $(\eta/\eta_0 - 1)/\sqrt{c}$  against  $\sqrt{c}$ , where " $c$ " is the total concentration of electrolyte in gram moles per litre. In every case a straight line was obtained, showing the applicability of the equation. The coefficients " $A$ " and " $B$ " for any such mixture were determined as usual from the plot. Onsager and Fuoss's expectation, *viz.* the existence of a square root term in the viscosity-concentration relation of electrolytic mixtures, thus receives the first experimental verification. Of course, it has to be borne in mind that here, as in the case of single substances, the law is correct only for dilute solutions.



Another behaviour which has been noticed is that the value of "A" in case of a mixture of two electrolytes changes linearly with increase or decrease of the fractional molar concentration  $c/(c_1 + c_2)$  for one of the electrolytes. The following figure will make this point clear. As the lines obtained in the cases of sodium chloride-barium chloride and sodium chloride-magnesium chloride mixtures are similar, only one of them is given. The values of "A" for pure barium chloride and magnesium chloride are taken from a previous paper.<sup>11</sup>

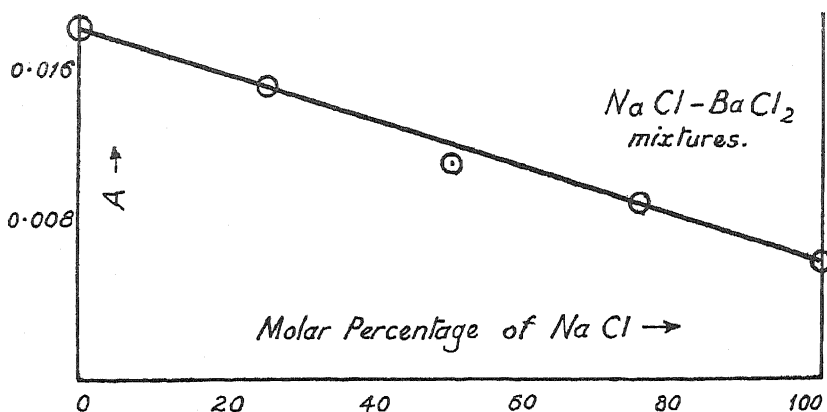


FIG. 1.

Thus, it follows that the value of "A" for any mixture containing the salts in the ratio  $c_1/c_2$  is given by the expression  $A = xA_1 + (1 - x)A_2$ , where  $x$ , i.e.  $c_1/(c_1 + c_2)$  is the fractional molar concentration of the first component and  $A_1$  and  $A_2$  are the values of "A" for the first and second component respectively.

Further work on the viscosity of mixed electrolytic solutions is in progress. The additivity of the values of "B" for mixtures will be discussed in a subsequent communication.

One of us (A. S. C.) wishes to record his thanks to the Government of Orissa for the award of a Research Scholarship.

### Summary.

1. Viscosity and density of mixed solutions of barium chloride with sodium chloride and magnesium chloride with sodium chloride in three different proportions as well as the values for pure sodium chloride are reported.

2. Onsager and Fuoss's limiting law for mixed ionic solutions has been established in these cases.

3. An equation of the Jones and Dole type has been applied with success to all the mixed solutions.

4. The coefficient of the square root term "A" has been shown to be a linear function of composition.

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# THE EFFECT OF HYDROCHLORIC ACID ON THE VISCOSITY OF BARIUM AND MAGNESIUM CHLORIDE SOLUTIONS.

By A. S. CHACRAVARTI AND B. PRASAD.

*Received 12th February, 1940.*

A good deal of work has been done on the viscosity of dilute solutions of electrolytes in order to test the Jones and Dole<sup>1</sup> equation :

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc,$$

as well as to compare the experimental value of " *A* " with that obtained from Falkenhagen and Vernon's<sup>2</sup> equation. Generally, the agreement has been good. Discrepancies have been observed in the cases of lanthanum chloride,<sup>3</sup> magnesium sulphate,<sup>3</sup> and nickel chloride.<sup>4</sup> When the salts are likely to be hydrolysed, some authors add a small amount of acid to repress hydrolysis. Thus, Cox and Wolfenden<sup>3</sup> added small amounts of hydrochloric acid to lanthanum chloride solutions. The present authors, while studying the effect of hydrochloric acid on the value of " *A* " for cadmium chloride,<sup>5</sup> found that the value of " *A* " was appreciably depressed in dilute solutions of hydrochloric acid. The Jones and Dole equation had not been expected to hold good with hydrochloric acid as solvent, as there is no allowance in Falkenhagen and Vernon's treatment for the electrical field due to charged ions from the solvent itself, even for the most dilute solutions. It was considered probable that the validity of the equation as well as the lowering of the value of " *A* " might be due to the formation of complex  $\text{CdCl}_4^{--}$  ions, and that the equation might break down if solutions of barium chloride or magnesium chloride in dilute hydrochloric acid were tried, as there was no possibility of complex ions being formed in these cases. With this object in view as well as with the idea of studying the change in the value of " *A* " with change in concentration of hydrochloric acid in case the Jones and Dole equation happened to hold good, it was decided to measure the viscosity of barium chloride and magnesium chloride in solutions containing hydrochloric acid, whose concentration was kept stationary for one set of measurements.

## Experimental.

The experimental procedure is the same as that described in previous papers.<sup>6</sup> The temperature was maintained at  $35^\circ \pm 0.005$  C. Double distilled water was used in all the experiments. No kinetic or surface tension correction was necessary with the viscometer used. The length of the capillary tube of the viscometer was 10 cm., its diameter 0.028 cm.,

<sup>1</sup> Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

<sup>2</sup> Falkenhagen and Vernon, *Phil. Mag.*, 1932, **14**, 537.

<sup>3</sup> Cox and Wolfenden, *Proc. Roy. Soc., A*, 1934, **145**, 475.

<sup>4</sup> Chacravarti and Prasad, *Trans. Faraday Soc.*, 1939, **35**, 1466.

<sup>5</sup> Chacravarti and Prasad, *J. Ind. Chem. Soc.*, 1938, **15**, 479.

<sup>6</sup> Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, **34**, 1139.

TABLE I.

Concentration.* (g. moles./ litre).	Density (g./c.c.).	Relative Viscosity (observed).	Relative Viscosity (calcu- lated).	Concen- tration (g. moles./ litre).	Density (g./c.c.).	Relative Viscosity (observed).	Relative Viscosity (calcu- lated).
<b>1. HCl; <math>\eta/\eta_0 = 1 + 0.006\sqrt{c} + 0.060c</math>.</b>				<b>8. MgCl<sub>2</sub> in 0.0025M. HCl;</b> $\eta/\eta_0 = 1.0005 + 0.014\sqrt{c} + 0.400c$ .			
0.0020	0.994087	1.0005	1.0004	0.0100	0.994861	1.0059	1.0059
0.0040	0.994127	1.0007	1.0006	0.0200	0.995669	1.0107	1.0105
0.0070	0.994170	1.0007	1.0009	0.0300	0.996467	1.0147	1.0149
0.0100	0.994233	1.0010	1.0012	0.0400	0.997239	1.0193	1.0193
0.0150	0.994315	1.0018	1.0016	0.0500	0.998046	1.0238	1.0236
0.0500	0.994949	1.0047	1.0044				
0.1000	0.995834	1.0081	1.0079				
<b>2. BaCl<sub>2</sub> in 0.0020M. HCl;</b> $\eta/\eta_0 = 1.0004 + 0.014\sqrt{c} + 0.240c$ .				<b>9. MgCl<sub>2</sub> in 0.0050M. HCl;</b> $\eta/\eta_0 = 1.0007 + 0.011\sqrt{c} + 0.415c$ .			
0.0025	0.994503	1.0015	1.0018	0.0100	0.994866	1.0059	1.0060
0.0050	0.994969	1.0026	1.0027	0.0200	0.995665	1.0109	1.0106
0.0150	0.996711	1.0062	1.0058	0.0300	0.996456	1.0149	1.0151
0.0250	0.998463	1.0087	1.0087	0.0400	0.997251	1.0195	1.0195
0.0400	1.001101	1.0126	1.0129	0.0475	0.997831	1.0226	1.0228
<b>3. BaCl<sub>2</sub> in 0.0040M. HCl;</b> $\eta/\eta_0 = 1.0006 + 0.012\sqrt{c} + 0.260c$ .				<b>10. MgCl<sub>2</sub> in 0.0075M. HCl;</b> $\eta/\eta_0 = 1.0010 + 0.008\sqrt{c} + 0.430c$ .			
0.0010	0.994307	1.0013	1.0013	0.0100	0.994905	1.0060	1.0061
0.0040	0.994848	1.0023	1.0024	0.0200	0.995684	1.0110	1.0106
0.0100	0.995902	1.0044	1.0044	0.0300	0.996481	1.0153	1.0153
0.0180	0.997322	1.0071	1.0069	0.0400	0.997276	1.0194	1.0198
0.0250	0.998506	1.0090	1.0090	0.0500	0.998059	1.0240	1.0243
0.0400	1.001155	1.0134	1.0134				
<b>4. BaCl<sub>2</sub> in 0.0070M. HCl;</b> $\eta/\eta_0 = 1.0009 + 0.009\sqrt{c} + 0.280c$ .				<b>11. MgCl<sub>2</sub> in 0.0100M. HCl;</b> $\eta/\eta_0 = 1.0012 + 0.004\sqrt{c} + 0.445c$ .			
0.0025	0.994621	1.0023	1.0021	0.0025	0.994394	1.0022	1.0025
0.0050	0.995063	1.0031	1.0029	0.0100	0.995007	1.0061	1.0061
0.0150	0.996876	1.0060	1.0061	0.0150	0.995400	1.0080	1.0084
0.0250	0.998681	1.0096	1.0093	0.0200	0.995799	1.0109	1.0107
0.0400	1.001338	1.0137	1.0139	0.0300	0.996590	1.0153	1.0153
				0.0400	0.997396	1.0198	1.0198
<b>5. BaCl<sub>2</sub> in 0.0100M. HCl;</b> $\eta/\eta_0 = 1.0012 + 0.006\sqrt{c} + 0.270c$ .				<b>12. MgCl<sub>2</sub> in 0.0125M. HCl;</b> $\eta/\eta_0 = 1.0014 + 0.002\sqrt{c} + 0.450c$ .			
0.0010	0.994415	1.0014	1.0017	0.0100	0.994988	1.0064	1.0061
0.0025	0.994681	1.0021	1.0022	0.0200	0.995773	1.0107	1.0107
0.0040	0.994912	1.0025	1.0027	0.0300	0.996571	1.0153	1.0152
0.0075	0.995543	1.0040	1.0037	0.0400	0.997352	1.0195	1.0198
0.0150	0.996856	1.0060	1.0059	0.0500	0.998136	1.0239	1.0243
0.0250	0.998614	1.0086	1.0089				
0.0400	1.001232	1.0132	1.0132				
<b>6. BaCl<sub>2</sub> in 0.0150M. HCl;</b> $\eta/\eta_0 = 1.0016 + 0.322c$ .				<b>13. MgCl<sub>2</sub> in 0.0500M. HCl;</b> $\eta/\eta_0 = 1.0044 + 0.430c$ .			
0.0025	0.994746	1.0024	1.0024	0.0100	0.995648	1.0089	1.0087
0.0050	0.995223	1.0030	1.0032	0.0200	0.996434	1.0130	1.0130
0.0150	0.997007	1.0065	1.0064	0.0300	0.997236	1.0174	1.0173
0.0250	0.998839	1.0101	1.0097	0.0400	0.998029	1.0215	1.0216
0.0400	1.001534	1.0141	1.0145	0.0500	0.998784	1.0257	1.0259
<b>7. BaCl<sub>2</sub> in 0.0500M. HCl;</b> $\eta/\eta_0 = 1.0044 + 0.295c$ .							
0.0010	0.995132	1.0048	1.0047				
0.0040	0.995659	1.0060	1.0056				
0.0075	0.996251	1.0067	1.0066				
0.0150	0.997587	1.0090	1.0088				
0.0250	0.999317	1.0117	1.0118				
0.0400	1.001954	1.0159	1.0162				

\* For (1)—of HCl; for (2)-(7)—of BaCl<sub>2</sub>; for (8)-(13)—of MgCl<sub>2</sub>.

and the approximate time of efflux for water was 29 minutes. Three readings for the time of flow generally agreeing within 0.2 sec. were taken with a Venner time switch marked off in tenths of seconds. The mass of a definite volume of the solution was determined in a pycnometer (about 64 c.c.), described before.<sup>4</sup> The density figures are results of two determinations, the weights being reduced to vacuum as described in a previous communication.<sup>7</sup> In every case, relative viscosity  $\eta/\eta_0$  (viscosity of solution/viscosity of water) was calculated as usual. Viscosity is accurate to 3 parts in 10,000 and density 16 in a million.

The  $\text{BaCl}_2$  used was Merck's *pro-analysi* quality,  $\text{MgCl}_2$  was Merck's reagent quality, and  $\text{HCl}$  was Schering-Kahlbaum's *pro-analysi* quality. A stock solution was prepared in each case whose strength was found gravimetrically. This solution was diluted to the proper concentrations. The results are given in the tables on opposite page.

### Discussion.

In the case of hydrochloric acid, "A" and "B" are obtained by plotting  $(\eta_{\text{HCl}}/\eta_0 - 1)/\sqrt{c}$  against  $\sqrt{c}$ . The intercept on the ordinate gives "A" and the slope of the straight line gives "B".

In case of barium and magnesium chloride solutions in presence of a fixed concentration of hydrochloric acid  $(\eta/\eta_0 - \eta_{\text{HCl}}/\eta_0)/\sqrt{c}$  plotted against  $\sqrt{c}$  gives straight lines. Hence, these results can be represented by an equation of the same kind as in aqueous solutions;

$$\eta/\eta_0 = \eta_{\text{HCl}}/\eta_0 + A\sqrt{c} + Bc.$$

Only "1", the relative viscosity of water is replaced by  $\eta_{\text{HCl}}/\eta_0$ , the relative viscosity of the hydrochloric acid solution, that is the solvent

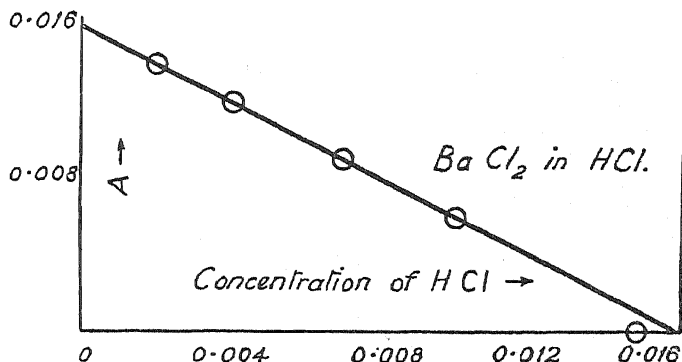


FIG. 1.

in these cases. "A" and "B" in acid solutions are found as in aqueous solutions. As for the value of  $\eta_{\text{HCl}}/\eta_0$  (i.e., the relative viscosity of the hydrochloric acid solution), it was calculated by means of the "A" and "B" constants for hydrochloric acid, which were obtained from the measurements on pure HCl solutions given in the table.

The surprising result that we get is that the Jones and Dole equation holds good even when dilute solutions of hydrochloric acid are used as solvents. The electrical field due to the ions from the acid does not make the Jones and Dole equation inapplicable. The equation holds

good, but the value of " $A$ " steadily decreases as the concentration of hydrochloric acid increases, as is seen in the figure. As the lines obtained for barium chloride and magnesium chloride are similar, only one of them is shown. It can be seen from the figure that the decrease is linear up to a certain concentration of hydrochloric acid beyond which " $A$ " becomes zero.

The value of " $A$ " extrapolated to zero concentration of acid is in fair agreement with the experimental <sup>4</sup> as well as the theoretical <sup>2</sup> value.

	Theoretical.	Experimental.	Extrapolated.
" $A$ " for $\text{BaCl}_2$	0.015	0.018	0.016
" $A$ " for $\text{MgCl}_2$	0.017	0.017	0.017

This behaviour may be utilised in determining the value of " $A$ " for salts which hydrolyse in aqueous solution. The value of " $A$ " in aqueous

solution for these salts can be found indirectly by making measurements in hydrochloric acid solutions of several fixed concentrations and extrapolating the straight line obtained therefrom to zero concentration of acid. Some tri-univalent salts will be taken up to examine the possibility of this method.

One of us (A. S. C.) wishes to record his thanks to the Government of Orissa for the grant of a Research Scholarship.

### Summary.

The Jones and Dole type of equation is obeyed by barium chloride and magnesium chloride, if a dilute solution of hydrochloric acid is used as solvent instead of pure water. Of course, " $\tau$ "—the relative viscosity of water—has to be replaced by  $\eta_{\text{HCl}}/\eta_0$ , the relative viscosity of the hydrochloric acid solution which is used as solvent, the equation assuming the form:  $\eta/\eta_0 = \eta_{\text{HCl}}/\eta_0 + A\sqrt{c} + Bc$ .

The value of " $A$ " decreases linearly with increase in the concentration of the hydrochloric acid solution used as solvent up to a certain concentration where it becomes zero. Beyond this point, the value remains stationary at zero. The value of " $A$ " extrapolated to zero concentration of acids is in fair agreement with the experimental as well as the theoretical value.

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# AN ELECTRON DIFFRACTION STUDY OF THE SURFACE REACTION BETWEEN NICKEL OXIDE AND CORUNDUM.

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*Received 18th January, 1940.*

The structure and orientation of deposits of substances evaporated on to single crystal substrates have recently been the subject of some research. Most of the investigations have been devoted to the study of metallic films formed on ionic crystals. The present paper, however, is mainly concerned with an example of a kind of orientation not previously observed, namely that of a non-metallic film condensed on to a crystal not definitely ionic. The example is that of nickel oxide deposited on corundum single crystal surfaces. Interest in this was first aroused by the observation of some remarkable electron-diffraction patterns yielded by a specimen of corundum which had been used for certain experiments on the effect of heat on the structure of the polish layer. The patterns were then identified as being due to nickel oxide originating from a nickel wire support used during an experimental heat treatment. The orientation of the nickel oxide crystals was such as to suggest that the oxide had been formed prior to deposition, and that the corundum surface was in effect an active substrate in that it determined the nature of the orientation of the nickel oxide. In view of the dissimilarity of the two structures (NiO, face-centred cubic,  $a = 4.17$  Å., rocksalt structure;  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, rhombohedral,  $a = 5.13$  Å.,  $\alpha = 55^\circ 6'$ , hæmatite structure), and of the fact that the electron diffraction patterns indicated unusually well-defined orientations, it was decided to investigate the phenomenon in some detail.

## Experimental.

Although several other methods of growing orientated nickel oxide deposits on the corundum surfaces were tried, the most satisfactory consisted of heating in a Bunsen flame a helix of nickel wire wound round the specimen. About ten minutes' heating sufficed to produce a film which, though quite invisible, gave clear diffraction effects.

Grey-brown, semi-transparent deposits of nickel on corundum were obtained by heating a nickel filament in vacuo near the surface of the heated specimen. These films could readily be oxidised by heating in air, when they became transparent and colourless. Films of similar appearance, but consisting of a mixture of nickel and nickel oxide were obtained by evaporation in air at about  $10^{-2}$  mm. pressure.

The corundum crystals were in the form of rectangular blocks, each of which had one face highly polished. These faces were cut so that their normals were at approximately  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$ , or  $90^\circ$  to the optic axis. They yielded electron diffraction patterns of diffuse spots. After etching (with a mixture of concentrated nitric and sulphuric acids) or annealing at about

\* For Figs. 1-4 see Plate VII; Figs. 7, 8, 10, 11, 12 and 15 see Plate VIII, and Figs. 16-19 see Plate IX.

1000° C. these surfaces yielded the Kikuchi line patterns characteristic of well-formed single crystals.

A camera length of 22.5 cm. and various accelerating potentials near 50 KV. were used.

### Results.

Nickel films evaporated on to corundum were found to consist of completely random crystals, together with a few having one degree of orientation, that is one type of net plane being parallel to the surface but the crystals otherwise at random. Nickel oxide films prepared in the manner outlined above consisted mainly of crystals exhibiting two degrees of orientation, that is, having certain specific positions relative to the underlying crystal. Films of nickel on corundum heated in air became colourless and transparent, and were found to consist of unorientated nickel oxide. Films prepared in a very limited supply of air consisted of a mixed deposit of nickel and nickel oxide, of which the nickel was random, and the nickel oxide orientated. Hence it was clear that orientation in two dimensions of nickel oxide crystals on corundum is only possible when the deposit is built up from the vapour, *i.e.* molecule by molecule. Evidently the nature of the orientation observed in this case is determined by the crystal structure of corundum and its relationship to that of nickel oxide.

Of the eight polished corundum surfaces employed, five were crystallographically different and four approximated closely to important planes in the crystal. These planes were approximately the basal plane  $\{000,1\}$ , the prisms  $\{11\bar{2},0\}$ , and  $\{10\bar{1},0\}$ , and the rhombohedron  $\{10\bar{1},1\}$ . The fifth surface contained a basal axis of the crystal, and was inclined by about 30° to the basal plane.

The Kikuchi line pattern served for the accurate identification of the crystallographic directions of the corundum surfaces. Thus, if in the Kikuchi line pattern from a triclinic crystal having axes  $a$ ,  $b$ ,  $c$ , and inter-axial angles  $\alpha$ ,  $\beta$ ,  $\gamma$ , the trace of a lattice row  $[\lambda\mu\nu]$  approximately normal to the plate be chosen as origin, the trace of a plane  $(uvw)$  containing  $[\lambda\mu\nu]$  be taken as the  $x$ -axis and the normal to it as the  $y$ -axis, then the equation of the median of the pair of Kikuchi lines arising from the plane  $(hkl)$  is given by

$$Px + Ry + L = 0,$$

where

$$P = \frac{d_{uvw}}{V(\lambda h + \mu k + \nu l)} \begin{vmatrix} \lambda a^2 + \mu ab \cos \gamma & \mu b^2 + \nu bc \cos \alpha & \nu c^2 + \lambda ca \cos \beta \\ + \nu ca \cos \beta, & + \lambda ab \cos \alpha, & + \mu bc \cos \alpha \\ u & v & w \\ h & k & l \end{vmatrix}.$$

and

$$R = \frac{D_{\lambda\mu\nu} d_{uvw}}{V^2(\lambda h + \mu k + \nu l)} \left[ \sum_{abc} u h b^2 c^2 \sin^2 \alpha - \sum_{abc} (kw + lv) a^2 bc (\cos \alpha - \cos \beta \cos \gamma) \right];$$

and, further,

$L$  = camera length,

$V$  = volume of unit cell =  $abc\sqrt{1 - \Sigma \cos^2 \alpha + 2 \cos \alpha \cos \beta \cos \gamma}$ ,

$d_{uvw}$  = net plane spacing of  $(uvw)$

$$= V / \sqrt{\Sigma u^2 b^2 c^2 \sin^2 \alpha - \Sigma 2uvw a^2 bc (\cos \alpha - \cos \beta \cos \gamma)},$$

and  $D_{\lambda\mu\nu}$  = spacing of lattice row  $[\lambda\mu\nu] = \sqrt{\Sigma \lambda^2 a^2 + 2 \Sigma \lambda \mu \nu bc \cos \alpha}$ .

In the case of corundum it is simpler to use a hexagonal unit cell,

$$a = b, c/a = c_0, \alpha = \beta = 90^\circ, \gamma = 120^\circ.$$

$$\text{Hence } P = \begin{vmatrix} \lambda - \frac{1}{2}\mu & \mu - \frac{1}{2}\lambda & \nu c_0^2 \\ u & v & w \\ h & k & l \end{vmatrix} \div (\lambda h + \mu k + \nu l) \sqrt{(u^2 + uv + v^2)c_0^2 + \frac{3}{4}w^2}.$$

$$\text{and } R = \frac{2\sqrt{\lambda^2 - \lambda\mu + \mu^2 + \nu c_0^2} \left[ u(h + \frac{1}{2}k) + v(k + \frac{1}{2}h) + \frac{3}{4}w\frac{l}{c_0^3} \right]}{(\lambda h + \mu k + \nu l) \cdot \sqrt{3} \cdot \sqrt{u^2 + uv + v^2 + \frac{3}{4}\frac{w^2}{c_0^3}}}.$$

For a prism face  $(11\bar{2}, 0)$  and the  $[001]$  azimuth

$$P = \frac{c_0(k - h)}{\sqrt{3} \cdot l},$$

$$R = \frac{(h + k)c_0}{l}.$$

The equation of the median of a pair of Kikuchi lines in the pattern (Fig. 18) is thus

$$(k - h)x + \sqrt{3}(k + h)y + \sqrt{3} \cdot lL/c_0 = 0.$$

The first surface used was within  $2^\circ$  of the prism face  $(11\bar{2}, 0)$ , and Figs. 1 and 3 are electron diffraction patterns from nickel oxide films deposited thereon. Fig. 1 was obtained with the beam in the direction of the  $c$ -axis azimuth, and similar patterns occurred at each  $60^\circ$  azimuth from this direction, while the pattern (Fig. 3), was obtained at  $30^\circ$ ,  $90^\circ$ , etc. The principal spot pattern can readily be indexed from the diagrams, Figs. 2 and 4. These patterns indicate that the nickel oxide crystals are for the most part orientated with  $\{111\}$  planes parallel to the prism face, and  $\langle 11\bar{2} \rangle$  lattice rows parallel to the  $c$ -axis of the corundum. Two equivalent orientations fulfil these conditions, and the superposition of the two corresponding patterns in each azimuth results in the patterns shown. In Fig. 1 the spots from crystals in the two orientations coincide in the zero-, third-, etc., order Laue zones. Fig. 2 is the index diagram corresponding to Fig. 1, and

$$\begin{aligned} \mp 2H' &= h - k, \\ K' &= h + k + l, \\ \pm 2L' &= h + k - 2l; \text{ and} \end{aligned}$$

Fig. 4 is the index diagram of the pattern Fig. 3,

where

$$\begin{aligned} \pm 2H' &= h + k - 2l, \\ K' &= h + k + l \\ \pm 2L' &= h - k. \end{aligned}$$

A second prism face cut less accurately than the first was also used. In this case the  $c$ -axis was inclined by about  $6^\circ$  to the surface (Fig. 18). Again a similar orientation was obtained, the  $\{111\}$  planes of the nickel oxide being parallel to the prism face, and not to the surface of the specimen.

It will be noticed that there is present in Fig. 1 a faint pattern of spots similar to the pattern of strong spots in Fig. 3, and *vice versa*; thus some of the nickel oxide crystals are orientated with the  $\{111\}$  planes parallel to the prism face and the  $\langle 11\bar{0} \rangle$  lattice row parallel to the  $c$ -axis, *i.e.* at  $90^\circ$  to the prevalent orientation. Furthermore, there are present a series of what are apparently very faint half-order diffractions, which are slightly drawn out towards the shadow edge. A complete explanation of the appearance of these will be given subsequently. Again in Fig. 3 there are diffractions for which  $H' = 0, 6, 12$ , etc., when  $K' = 1, 2, 4, 5, 7, 8$ , etc., and for  $H' = 1, 2, 4, 5, 7, 8$ , etc., when  $K' = 0, 3, 6$ , etc. These give values of  $h, k$ , and  $l$  which differ by  $\frac{1}{2}$  from integers. Thus these might at first sight be supposed to be due to some kind of submicroscopic twinning, as has been postulated in the case of silver films on rocksalt,<sup>1</sup> but if this were the case, certain of them, for example those in the plane of incidence, should appear in Fig. 1 (which was obtained from the same

<sup>1</sup> G. Menzer, *Z. Krist.*, 1938, **99**, 378; O. Goche and H. Wilman, *Proc. Physic. Soc.*, 1939, **51**, 625.



specimen) whereas they are absent. A satisfactory explanation of their appearance in Fig. 3 is provided by "double diffraction," the re-diffraction by a crystal in one orientation of a beam arising from diffraction by a crystal in the other orientation. It is worthy of note that in the patterns from silver films condensed on to rocksalt those of the "extra" spots which are not due to simple twinning may be explained in the same way.

In Fig. 5 the arrangement of lattice points in the junction planes of the two crystals are superposed. The corundum lattice is regarded as being "body-centred" rhombohedral; this is not quite accurate, since the two molecules in this "body-centred" unit cell are rotated with respect to one another by  $180^\circ$  about the three-fold axis. It will be seen from the figure that there is no close fit of the two lattices along the plane of junction. The reason for the similarity in dimensions between the spot patterns of

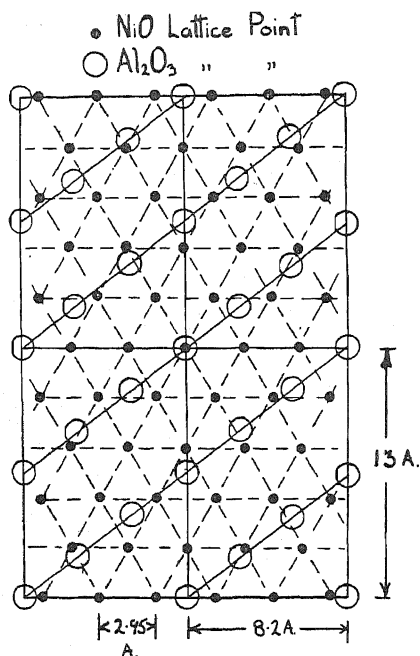


FIG. 5.—(111) net of nickel oxide and  $(11\bar{2},0)$  net of corundum in their relative positions.

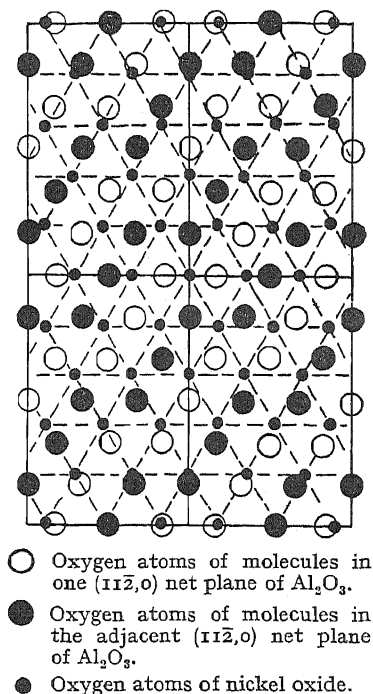


FIG. 6.—As Fig. 5, but showing the oxygen arrangement of corundum.

the nickel oxide and of the corundum in the  $[001]$  azimuth of the latter lies in the coincidence in spacing of the net planes parallel to the surface and to the plane of incidence in the two structures. Thus for corundum the spacings of the  $(11\bar{2},0)$  and  $(10\bar{1},0)$  planes respectively are 2.38 and 1.37 Å., while for nickel oxide the spacings of the  $\{111\}$  and  $\{1\bar{1}0\}$  planes which are parallel to these are 2.41 and 1.47 Å. respectively. If the arrangement of oxygen atoms in a  $(11\bar{2},0)$  plane is considered, it is found that they form a network similar to that in the octahedral plane of nickel oxide (Fig. 6), and the two structures fit by virtue of this similarity.

A peculiar feature of this case of orientation is that although the two predominant orientations of the nickel oxide crystals are equivalent, there is a decided tendency for one of them to occur more strongly than the other. This was especially the case in very thin films; moreover, it is always the same orientation that is preferred on a given specimen.

Figs. 7 and 8 are diffraction patterns obtained from a nickel oxide film formed on the basal plane (000,1) of corundum. It was immediately apparent that these patterns were similar to Figs. 1 and 3. In this case the {111} plane of nickel oxide is parallel to the basal plane and the  $\langle 11\bar{2} \rangle$  lattice row parallel to the  $a$ -direction of the corundum. Extra diffractions similar to those obtained from films on the prism face are also present, but the apparently half-order diffractions are fainter. There are also present continuous rings, probably as a result of incomplete annealing of the substrate crystal. The two lattices fit fairly well along the junction plane, as shown in Fig. 9.

The two orientations of nickel oxide on corundum so far described, *viz.*, those on the prism  $\{11\bar{2},0\}$  and the base  $\{000,1\}$  are entirely different as regards crystallographic direction. Thus unlike the epitaxy of sodium nitrate on calcite,<sup>2</sup> there is no single definite orientation of deposit and substrate which is independent of the direction of the substrate surface. It is therefore of interest to note that both of these orientations can occur on the surfaces inclined by as much as  $30^\circ$  to the plane defining the orientation. For example, on a surface containing an  $a$ -axis of the corundum, but inclined by about  $30^\circ$  to the basal plane, nickel oxide films are orientated in exactly the same way as on the basal plane. When the electron beam is parallel to the  $a$ -axis, therefore, a diffraction pattern (Fig. 12) similar to Fig. 7, is obtained, except that it is tilted by  $30^\circ$  to the shadow edge. Further, the orientation observed on the prism  $\{11\bar{2},0\}$  also occurs on the prism  $\{10\bar{1},0\}$ . Nickel oxide crystals with octahedral planes parallel to the two prisms of the type  $\{11\bar{2},0\}$  adjacent to and making angles of  $30^\circ$  with surface occur. Thus there are present four positions with the  $\langle 11\bar{2} \rangle$  lattice row of nickel oxide parallel to the  $c$ -axis of the corundum. It was observed that both on the plane inclined by  $30^\circ$  to the basal plane and on the prism  $\{10\bar{1},0\}$  the patterns consisted of arcs rather than spots.

One other kind of orientation of nickel oxide on corundum was observed. A surface cut so that it was inclined by about  $65^\circ$  to the basal plane, and containing an  $a$ -axis of the crystal was found to be about  $5^\circ$  from the rhombohedron  $\{10\bar{1},1\}$ . Nickel oxide films crystallised on this surface with  $\{110\}$  planes parallel to the rhombohedron. Symmetrical spot patterns were obtained in both the  $a$ -axis azimuth and the azimuth normal to it. At azimuths  $27\frac{1}{2}^\circ$  from the  $a$ -axis, *i.e.*  $90^\circ$  from the rhombohedral edges, almost symmetrical patterns were obtained (*e.g.*, Fig. 10). This

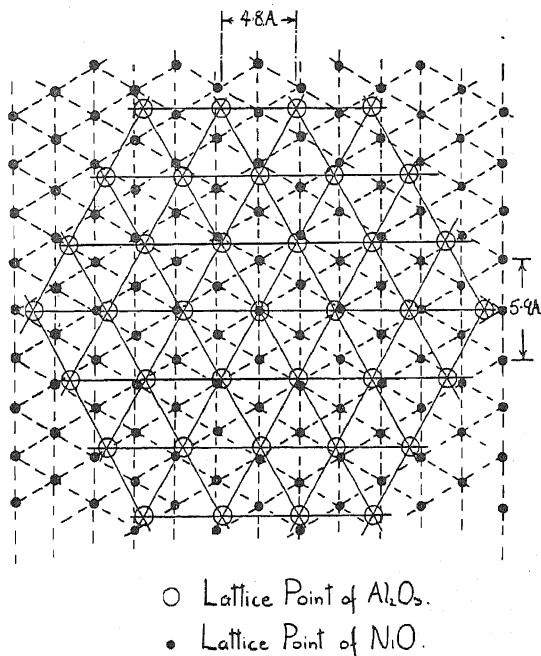


FIG. 9.—(111) net of nickel oxide and (000,1) net of corundum in their relative positions.

<sup>2</sup> Finch and Whitmore, *Trans. Faraday Soc.*, 1938, 34, 640.

pattern consists of a square and a hexagonal pattern of spots (from the  $\langle 001 \rangle$  and  $\langle 1\bar{1}1 \rangle$  azimuths of nickel oxide respectively) superposed (Fig. 11). The spots in the zero-order Laue zone not thus accounted for are due to

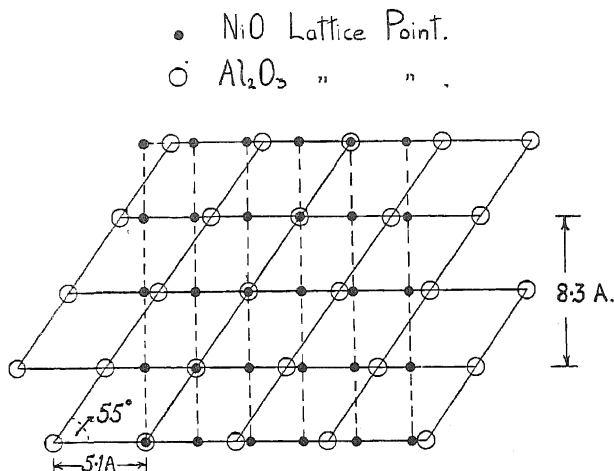


FIG. 13.— $\{110\}$  net of nickel oxide and  $\{10\bar{1},1\}$  net of corundum in their relative positions.

double diffraction. Thus the  $\langle 001 \rangle$  and  $\langle 1\bar{1}1 \rangle$  lattice rows of the nickel oxide are perpendicular to the rhombohedral edge of the corundum. Actually there are four orientations fulfilling these conditions, but the angle between the lattice rows  $\langle 001 \rangle$  and  $\langle 1\bar{1}1 \rangle$  in the  $\{110\}$  plane of nickel oxide is  $54^\circ 55'$ , only  $12'$  less than the rhombohedral angle of corundum. Thus in effect there are only two orientations; one of these is shown in Fig. 13, the other being symmetrically placed with respect to the corundum. The  $\langle 1\bar{1}0 \rangle$  and  $\langle 1\bar{1}2 \rangle$  lattice rows are parallel to the rhombohedral edges. Their spacings are 2.95 Å. and 5.12 Å. respectively, as compared with the rhombohedral primitive translation of corundum of 5.13 Å. Thus, on the rhombohedron there is a close fit of the lattices along the junction plane, both in angle and dimensions.

The above experiments show that corundum is an active substrate for nickel oxide. Three different relative orientations of the two lattices were observed. In two of these there was a close coincidence of the lattice dimensions in directions parallel to the planes defining the orientation. In the third case a fit of the two structures could be obtained by a consideration of the arrangements of their oxygen atoms. Fig. 14 shows a corundum crystal which has all the faces described above, approximately the basal plane  $c$   $\{000,1\}$ , the prisms  $a$   $\{11\bar{2},0\}$ , and  $m$   $\{10\bar{1},0\}$ , and the

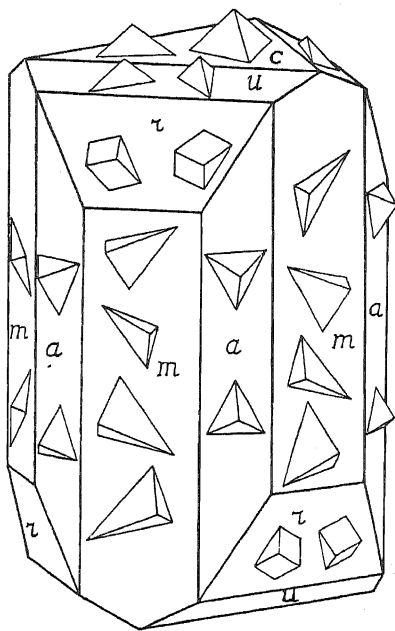


FIG. 14.—Diagram of relative orientations of nickel oxide and corundum.

rhombohedra  $\nu$   $\{10\bar{1},1\}$  and  $u$   $\{10\bar{1},4\}$ . Cubic crystals of nickel oxide are shown in positions representing the orientations found. The results are summarised in Table I.

TABLE I.

Indices of Corundum Faces.	Orientation of Nickel Oxide.	Description of Typical Pattern.
$\{11\bar{2},0\}$	$\{111\}$ NiO parallel to $(11\bar{2},0)$ $Al_2O_3$ . $\langle 11\bar{2} \rangle$ NiO parallel to $[001]$ $Al_2O_3$ , also traces of $\langle 1\bar{1}0 \rangle$ NiO parallel to $[001]$ $Al_2O_3$ .	Sharp spots, thin films usually formed, and pattern due to substrate showing; (Figs. 1 and 3)
$\{10\bar{1},0\}$	$\{111\}$ NiO parallel to $(11\bar{2},0)$ $Al_2O_3$ . $\langle 11\bar{2} \rangle$ NiO parallel to $[001]$ $Al_2O_3$ .	Arced spots with thicker films.
$\{000,1\}$	$\{111\}$ NiO parallel to $(000,1)$ $Al_2O_3$ . $\langle 11\bar{2} \rangle$ NiO parallel to $[001]$ $Al_2O_3$ .	Sharp spots on faint, continuous rings. Fairly thick films formed. (Figs. 7 and 8).
$\{10\bar{1},4\}$ approx., i.e., plane at $30^\circ$ to basal plane containing an $a$ -axis.	$\{111\}$ NiO parallel to $(000,1)$ $Al_2O_3$ . $\langle 11\bar{2} \rangle$ NiO parallel to the $[001]$ $Al_2O_3$ .	Sharp spots and faint arcs. Fairly thick films. (Fig. 12).
$\{10\bar{1},1\}$	$\{110\}$ NiO parallel to $(10\bar{1},1)$ $Al_2O_3$ . $\langle 1\bar{1}0 \rangle$ parallel to the rhombohedral edge $[1\bar{2}1]$ .	Pattern of short arcs and spots. Fairly thick films. (Fig. 10).

On the prism  $a$   $\{11\bar{2},0\}$  only the predominant orientations are shown. Of the extra diffractions appearing in most of the patterns, many may be explained by double diffraction, and the remainder consisted of apparently half-order diffractions. A closer examination of these "half-order" spots show that in every case they are part of a pattern of spots exactly similar to the normal nickel oxide pattern except that it is about 3 per cent. more than half the size. Thus there is present in these films a substance of cubic structure for which the unit cell has  $a = 8.1$  Å. This immediately suggests a substance of the spinel type. Of the possible substances having this structure, only nickel aluminate,  $NiAl_2O_4$ , can be looked for under the conditions of the experiment. Moreover, its known lattice dimensions agree very well with the dimensions of the patterns in question. The appearance of the nickel spinel pattern, together with the fact that its diffraction spots sometimes show refractive index effects suggests that the formation of orientated nickel oxide films may depend on the presence of a junction layer of the mixed oxide.

In general, it was found that the more rapid the evaporation, the less the proportion of nickel aluminate. It was noted that thin films yielding little or no trace of nickel aluminate were just as highly orientated as those in which there was a large proportion of this substance. The tendency to form the spinel was particularly noticeable on the prism  $\{11\bar{2},0\}$  and it was also observed that the thickness of the nickel oxide film formed in a given time was less on this face than on any other.

Heating in air at  $900^\circ$  C. of specimens of nickel oxide on corundum caused the general fading of the nickel oxide pattern and the corresponding strengthening of the nickel spinel pattern (see Figs. 16 and 17,

and compare with Figs. 7 and 8). On all faces the spinel had the same orientations as the nickel oxide, except that on the prism  $\{11\bar{2}, 0\}$  only one of the two principal orientations occurred. The spots due to spinel usually had the same form as those due to the nickel oxide; thus Fig. 17 consists of arced spots, as does Fig. 8. On the prism face  $\{11\bar{2}, 0\}$ , however, the spots due to the spinel were extended towards the shadow edge, whereas the nickel oxide spots were more or less circular. Also in this case there were found to be anomalous Kikuchi lines in the corundum Kikuchi line pattern which accompanied the cross-grating spot patterns (Fig. 19). It is possible that these were due to double diffraction, but if this were so, it would have to be supposed that a beam corresponding to each point of one of the normal Kikuchi lines acted as a primary beam for a cross-grating pattern of nickel aluminate spots. This would fail to explain the considerable intensity of the extra lines, and so it seems that they may be the  $111$  bands of the spinel on the surface.

Continued heating of these specimens at  $900^\circ$  C. did not result in any decrease in intensity of the nickel spinel pattern; moreover, the thickness of the spinel film was certainly not less than that of the original nickel oxide film, as adjudged by the appearance of the background pattern of the corundum Kikuchi lines. Random nickel oxide films could be prepared on corundum by evaporation from a film with the substrate at  $500^\circ$  C. or less. When the specimens were strongly heated in air, no nickel aluminate rings appear, but the ring pattern of the nickel oxide gradually decreased in intensity and at the same time the intensity of the spot pattern of the corundum increased.

Thus nickel oxide once orientated on to corundum cannot easily be removed by evaporation, and once all the nickel oxide is combined with the alumina, further heating has no effect and does not cause the nickel oxide to diffuse right into the corundum. It appears that the reaction  $\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$  can only occur when the nickel oxide is orientated with respect to the corundum. Arcs due to the nickel spinel were always sharp, and corresponded to the same lattice dimensions ( $a_0 = 8.08$  Å.) These observations indicate that there is no phase of variable lattice dimensions.

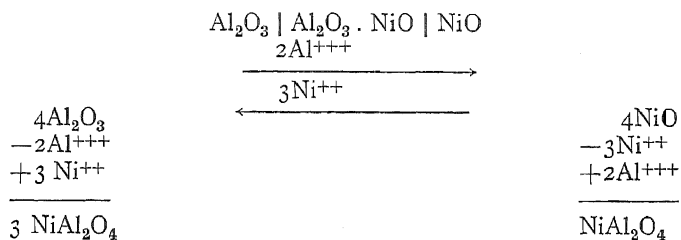
### Discussion.

It is evident that the prism face of corundum behaves differently from other faces in respect of the orientation of nickel oxide crystals by condensation from the vapour on the surface. The differences may be summarised as follows:

- (i) The orientation of the nickel oxide and of the spinel is most perfect on the prism face  $\{11\bar{2}, 0\}$ , sharp spot patterns without arcs or rings usually being obtained.
- (ii) A considerable proportion of the nickel spinel is always present in the films on the prism face.
- (iii) The rate of adsorption of nickel oxide is slower on the prism face.
- (iv) There is no close lattice fit of the nickel oxide and corundum structures on this plane, although the two structures fit fairly well as regards the oxygen structures.
- (v) The spinel orientation does not entirely follow that of the nickel oxide crystals on this face, only one of two equivalent orientations being present (Fig. 15).
- (vi) The diffraction spots due to the spinel differ from those of the nickel oxide in showing an extension perpendicular to the shadow edge, due to refraction of the diffracted beams.

It appears that there is some fundamental difference in the nature of the orientating influences on the prism faces from that on other corundum surfaces. The two kinds of orientations observed on faces other than the prisms may be regarded as being of the Royer type, in that the lattices fit on the plane of junction without the formation of an intermediate mixed oxide, *i.e.* spinel, layer.

The probable mechanism of the surface reaction on the basal plane of corundum may be pictured from a consideration of the structural relations at the interface. The oxygen atoms in the corundum structure consist approximately of plane hexagonally packed layers perpendicular to the three-fold axis, the mean oxygen spacing being 2.75 Å. The oxygen atoms in the nickel oxide structure also consist of hexagonally packed layers with packing distance = 2.95 Å. Thus the nickel oxide may be regarded as sharing an oxygen layer with the substrate. The oxygen structure of spinel is identical with that of nickel oxide except that the dimensions of the unit cell are slightly smaller, the oxygen atom separation being 2.85 Å. Thus the formation of the spinel may be pictured as interdiffusion of the metal ions in the two lattices involving only a slight change in the dimensions of the stationary oxygen framework. The reaction then proceeds according to the following scheme:



A reaction between nickel and aluminium oxides in the solid state has been observed by Hedvall.<sup>3</sup> The mechanism of the formation of the spinel structure has been discussed by Barth and Posnjak,<sup>4</sup> and a summary on this and related subjects is given by Wagner.<sup>5</sup> The investigation of Wollan<sup>6</sup> on the electron distribution in the magnesium oxide lattice indicated that lattices of the MgO type are non-ionic. Some experiments by the authors (not yet published) on the orientation of silver films condensed on to magnesium oxide suggest, however, that the latter becomes ionic, at least to some extent, at temperatures above 500° C.

As has been mentioned, the array of oxygen atoms in a plane {112,0} of corundum is approximately hexagonal (Fig. 6). Half of these atoms, however, belong to molecules in one layer and half to the layer below. Thus, if corundum be regarded as a molecular structure, the prism face would contain only half of the oxygen atoms shown in the figure, and unless the spaces were filled with adsorbed oxygen atoms, the "sharing" of an oxygen layer with the nickel oxide crystals would not occur on this surface. It is evident, however, that in this case also a relatively slight change in the oxygen structure of the corundum is necessary for the formation of spinel. It is possible that

<sup>3</sup> Hedvall, *Z. anorg. Chem.*, 1915, **92**, 381.

<sup>4</sup> T. W. Barth and E. Posnjak, *Z. Krist.*, 1932, **82**, 325.

<sup>5</sup> C. Wagner, *Angewandte Chemie*, 1936, **49**, 735.

<sup>6</sup> E. O. Wollan, *Physic. Rev.*, 1930, **35**, 1019.

the formation of an orientated film of nickel oxide on the prism face depends on the formation of a thin layer of spinel by the first few molecular layers of nickel oxide.

The reaction scheme shown above satisfactorily accounts for the ease of formation of the orientated spinel layer on the (000,1) plane of corundum. On the other faces of the corundum there should be formed a double layer of spinel, one layer having the orientation of the nickel oxide, and beneath that a layer having an orientation depending solely on that of the aluminium oxide. The picture is unsatisfactory because (i) no trace of a second kind of orientation of spinel was found, (ii) if nickel and aluminium ions can diffuse across the spinel-corundum interface there appears to be no reason why the reaction should cease when all the nickel oxide is combined, and (iii) it affords no reasonable explanation as to why the spinel takes up only one of the two nickel oxide orientations on the prism face.

These difficulties can be resolved to some extent if it be supposed that diffusion can only occur in the spinel lattice. In this case only those metal ions in the uncombined oxides that are immediately adjacent to the spinel layer could leave the oxide lattice to diffuse into the spinel. The oxygen atoms "freed" by this process would, by a very slight rearrangement, become part of the spinel oxygen lattice and the slight excess of metal ions provided by the diffusion process would take up their appropriate positions in the extended spinel lattice. According to this model the spinel lattice once formed would continue to grow at the expense of both the nickel and aluminium oxides without changing in orientation. The reason that the initial layer of spinel takes up the orientation of the nickel oxide rather than that of the corundum may well be the identity of the oxygen lattices of nickel oxide and spinel.

### Summary.

The structure, orientation and spinel-formation of crystalline nickel oxide films condensed on to heated corundum single crystals have been studied by electron diffraction.

It was found that the nickel oxide crystals take up, with respect to the substrate crystal, certain special orientations according to the crystallographic direction of the corundum surface. These orientations have been explained in terms of geometrical similarities between the two crystals in important planes near the junction surface. The nickel oxide was shown to react slowly at about 900° C. with the corundum to form nickel spinel, which takes up orientations similar to those of the nickel oxide. Certain of these results can be explained on the assumption that the spinel lattice is the only one of the three in which appreciable diffusion of metal ions can occur.

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# THE DIELECTRIC CONSTANT OF DIAMOND.

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An investigation of the optical and photoelectric properties of diamond<sup>1,2</sup> has disclosed the existence of at least two forms (types 1 and 2), and a preliminary measurement of the dielectric constant was reported in the first of these publications. It was established that both types of diamond had the same dielectric constant within experimental error, but the absolute value could not at that time be determined with the accuracy desired, owing to the lack of a suitable standard micro-condenser.

Reference to the literature reveals a wide range of values. Pirani<sup>3</sup> gives a value of 16.5, Schmidt<sup>4</sup> a value of 5.5, Coehn and Raydt<sup>5</sup> values between 5.18 and 8.0. More recently, Whitehead and Hackett<sup>6</sup> have found a value of  $5.7 \pm 2\%$  over the frequency range 300 c./sec. to 1.6 Mc./sec., with a most accurate determination of 5.66 at 800 c./sec. and 27.8° C.

## Part I. Method of Measurement Involving Diamond/Air Capacity Change.

The first apparatus was of the resonance type operating at a frequency of approximately 1 Mc./sec., and is fully described elsewhere.<sup>7</sup> For use with solids a micrometer condenser cell, Fig. 1, was constructed from a micrometer head, circular parallel brass plates 16 mm. diameter being used for the electrodes. Unworked diamonds, such as were employed here, are usually available as cleavage plates up to a few mm. in thickness and less than 1 sq. cm. in area, and can be sandwiched between the plates of the micrometer cell. In the resonance apparatus, variation in the capacity of the condenser due to introduction of the solid caused a change in the rectified current of the valve-voltmeter, and the actual capacity change was found by adjustment of a standard variable condenser (Sullivan, 70-1200  $\mu\text{F}$ ) in series with a small fixed condenser (10-20  $\mu\text{F}$ ) until the original current reading was established. The small fixed capacity

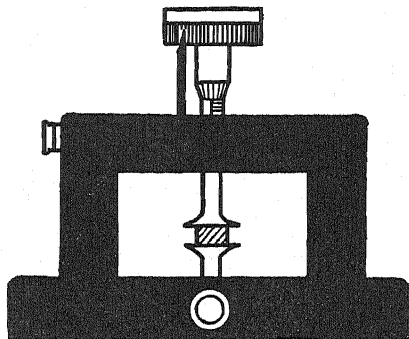


FIG. 1.

<sup>1</sup> Robertson, Fox and Martin, *Phil. Trans., A*, 1934, **232**, 463.

<sup>2</sup> Robertson, Fox, and Martin, *Proc. Roy. Soc., A*, 1936, **157**, 579.

<sup>3</sup> Pirani, *Dissertation*, Berlin (1903).

<sup>4</sup> Schmidt, *Ann. Physik*, 1903, **11**, 114.

<sup>5</sup> Coehn and Raydt, *ibid.*, 1909, **30**, 777.

<sup>6</sup> Whitehead and Hackett, *Proc. Physic. Soc.*, 1939, **51**, 173.

<sup>7</sup> Groves and Sugden, *J. Chem. Soc.*, 1934, 1094.



is chosen so that a considerable portion of the standard variable condenser is required to compensate for the capacity change in the cell, but the exact measurement of this small fixed capacity provides the chief difficulty associated with the method. In practice it was determined by varying the air capacity of the micrometer cell: the capacity change on varying the air gap from  $t_1$  to  $t_2$  cm. is  $\frac{A}{3 \cdot 6\pi} \left( \frac{1}{t_2} - \frac{1}{t_1} \right) \mu\text{F}$ , where  $A$  is the area of either electrode in  $\text{cm}^2$ .

This calibration was found to be somewhat in error owing to changes in stray capacities associated with the backs and edges of the brass electrodes, and it was decided that the construction of a standard micro-variable-condenser was the only satisfactory method of overcoming the difficulty. At this stage in the work a change in electrical apparatus was made.

### Description of Improved Apparatus.

This operated on the heterodyne principle at the same frequency as the first apparatus and made use of certain methods of frequency stabilisation; it was also equipped with a standard micrometer variable condenser of calibration constant  $1 \cdot 862 \mu\text{F}$  per cm. travel, the reading being estimated to  $10^{-4}$  cm., viz., about  $2 \times 10^{-4} \mu\text{F}$ .

A further refinement was the substitution of a cathode-ray oscillograph as a means of observing the heterodyne beat frequency, in place of the tuning fork methods usually employed in this type of work. The whole apparatus has been described in detail by one of us (L. G. G.),<sup>8</sup> in connection with the measurements of the electric moments of vapours. The cell, Fig. 1, was again used for the solids, but the increase in capacity caused by their insertion was measured by direct replacement with the micro-variable condenser, i.e.  $\frac{A}{3 \cdot 6\pi t}(\epsilon - 1) = \delta C$ , where  $A$  is the area of the solid ( $\text{cm}^2$ ),  $t$  its thickness (cm.), and  $\epsilon$  the dielectric constant. It is of interest to consider the possible error in the results due to an air film, assumed for simplicity to be uniform in thickness, at an insulator-electrode interface. If  $\delta t$  is the thickness of the air film, then from the theory of mixed dielectrics, the capacity change on introduction of the solid is:

$$\begin{aligned} & \frac{A}{3 \cdot 6\pi \{t + \delta t - t(1 - 1/\epsilon)\}} - \frac{A}{3 \cdot 6\pi (t + \delta t)} \\ &= \frac{A\epsilon}{3 \cdot 6\pi t} \left( 1 - \frac{\delta t}{t} \epsilon \right) - \frac{A}{3 \cdot 6\pi t} \left( 1 - \frac{\delta t}{t} \right) \text{ very nearly} \\ &= \frac{A}{3 \cdot 6\pi t} (\epsilon - 1) - \frac{A}{3 \cdot 6\pi t} \cdot \frac{\delta t}{t} (\epsilon^2 - 1) \text{ instead of } \frac{A}{3 \cdot 6\pi t} (\epsilon - 1). \end{aligned}$$

If the air film is 1% of the thickness of the solid, the value found for  $\epsilon$  will be  $(\epsilon - 1/\epsilon)\%$  low, and since the air film is likely to be much the same for thick or thin specimens, it is desirable, where controllable, to use as thick a plate of solid dielectric as will give a reasonable change in capacity of the cell.

### Measurements and Results.

Several specimens of diamond were available, and we would like here to express our thanks to Professor W. T. Gordon for the loan of these. Of the type 1 diamonds, figures are given in Table I for one only (Dr), this being the most suitable in form of those available. It was an equilateral triangular plate, of side about 10 mm. length, and 3.11 mm. in thickness. Others of this type, but with less suitable dimensions, gave

<sup>8</sup> Groves, *J. Chem. Soc.*, 1939, 1144.

similar values for  $\epsilon$ . Only one moderately suitable specimen of type 2 diamond (No. 2) could be obtained, but unfortunately had a stepped edge. This may be considered approximately as being composed of a plane parallel part of area  $A_1$  and a wedged portion of area  $A_2$ , Fig. 2, and the capacity change due to insertion between the electrodes can be shown to be nearly

$\frac{A_1}{3 \cdot 6 \pi t}(\epsilon - 1) + \frac{A_2}{3 \cdot 6 \pi t} \left[ \frac{\ln \epsilon}{1 - 1/\epsilon} - 1 \right]$ , from which  $\epsilon$  may be found. As it

is possible that the edge irregularities of the diamonds of both types, though inside the volume bounded by the cell plates, may cause some error in the measured values of  $\epsilon$ , it was thought advisable to check this point. Accurate glass models of the diamonds were made and their apparent values of  $\epsilon$  compared with an accurate value for the same glass in the form of regular plates. (The models were made by Mr. F. S. Bengt of this laboratory.)

The several ratios are as follows:—

$$\frac{\text{Capacity change for diamond No. 1}}{\text{Capacity change for glass model}} = 0 \cdot 789$$

$$\frac{\text{Capacity change for diamond No. 2}}{\text{Capacity change for glass model}} = 0 \cdot 813$$

$$\frac{\text{Measured } \epsilon \text{ for diamond No. 1}}{\text{Measured } \epsilon \text{ for glass of models}} = 0 \cdot 796$$

It thus appears that the dielectric constants directly measured for the two diamonds are satisfactory and that the difference between them is within the limits of experimental error;  $\epsilon$  for diamond No. 1, 5.26, is the value preferred since this diamond had the more regular form.

As a further check on the method, measurements were made on three plane parallel plates of fused silica, the individual values for which were in good mutual agreement. These results are included in Table I with those for the diamond  $D_1$ . The average result, 3.69, may be compared with Jaeger's<sup>9</sup> values 3.57-3.80 for six different methods.

TABLE I.

Substance.	$A$ (cm. <sup>2</sup> ).	$t$ (cm.)	$C$ ( $\mu\mu F.$ )	$\epsilon$ .	$\epsilon$ (Mean.)
Diamond $D_1$ . . .	0.598	0.311	0.725	5.26	3.69
Silica 1 . . . .	0.945	0.249	0.913	3.72	
„ 2 . . . . .	0.575	0.256	0.533	3.69	
„ 3 . . . . .	0.339	0.254	0.315	3.67	

## Part II.—Method of Measurement Involving Diamond/Liquid Capacity Change.

In view of the fact that our value of 5.26 for diamond differs considerably from 5.7 found by Whitehead and Hackett at our frequency of measurement, it was decided to repeat the determination with a liquid replacement method to eliminate air films, mentioned above as a source of error.

Briefly, this consists in measuring the dielectric constants of a range of liquids of lower and higher dielectric constant than that of the solid, alone

<sup>9</sup> Jaeger, *Dissertation*, Berlin (1917).

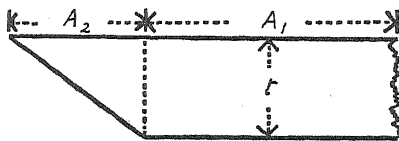


FIG. 2.

and with the solid immersed in them. If  $\epsilon_l$  is the dielectric constant of the liquid, and  $\epsilon_m$  the dielectric constant of the same liquid with the solid immersed in it, then the dielectric constant of the solid is given by that value of  $\epsilon_m$  which satisfies the relation  $\epsilon_m/\epsilon_l = 1$ . Accordingly, therefore, if such measurements are carried out with a range of liquids and  $\epsilon_m/\epsilon_l$  is plotted against  $\epsilon_m$  (abscissa), then the value of  $\epsilon_m$  corresponding with the point of intersection of the curve with the line  $\epsilon_m/\epsilon_l = 1$  gives the dielectric constant of the solid.

### Apparatus.

The improved apparatus described in Part I was used, except that a special micro liquid condenser (Fig. 3) replaced the micrometer cell.

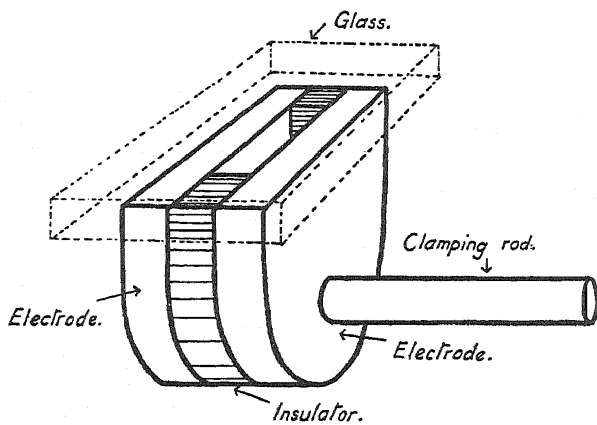


FIG. 3.

This liquid cell was made from two circular brass plates and a ring of synthetic resin about 3.5 cm. diameter. Both surfaces of the ring and the inner surfaces of the brass plates were polished flat. The inner diameter of the ring was 2 cm., its thickness about 4 mm., and the inner wall of the ring was carefully turned so that it made an angle of  $90^\circ$  with each inner surface of the brass

plates. The three components were assembled with a trace of fish glue and then bolted together with three bolts tapped into the insulator. The three bolts formed the corners of an equilateral triangle, two being inserted from one electrode and the third from the other. In either brass plate large clearance holes were drilled opposite the ends of the bolts to keep insulation high. The combination of electrodes and insulating ring was then sawn into unequal segments such that the larger provided a cell of vertical inner depth 1.3 cm., and of volume about 0.95 c.c. The cut surface of this cell was polished flat and was at right angles to the inner surfaces of the electrodes. A rectangular glass slab (6 cm.  $\times$  3 cm.  $\times$  4 mm.) with one face optically flat was used to cover the cell, being adjusted symmetrically over the cell aperture. A heavy brass rod provided a means of clamping the cell and was connected to earth; the other plate was joined by a rigid fine wire to the electrical apparatus. The completed cell provides a condenser of constant boundary conditions, the capacity changes of which when filled with an insulating liquid of dielectric constant  $\epsilon_l$  will be directly proportional to  $\epsilon_l - 1$ . To check this point, the replaceable capacity was determined by calibration with benzene at  $20^\circ$  C., and using the cell constant,  $C_0$ , so obtained, the dielectric constant of chlorobenzene at  $25^\circ$  C. was measured. The value used for benzene at  $20^\circ$  was 2.283 (Hartshorn and Oliver)<sup>10</sup> and the value obtained for chlorobenzene at  $25^\circ$  was 5.61; cf. Sugden's<sup>11</sup> value of 5.612 obtained by a method which gave results for benzene in agreement with Hartshorn and Oliver's figure at  $25^\circ$ . These measurements are set out in Table II.

<sup>10</sup> Hartshorn and Oliver, *Proc. Roy. Soc., A*, 1929, 123, 664.

<sup>11</sup> Sugden, *J. Chem. Soc.*, 1933, 773.

TABLE II.

$M_0$ (mm.).	$M_t$ (mm.)	$M_t - M_0$ (mm.)	$\delta C.$ ( $\mu\mu F.$ )	$C_0$ ( $\mu\mu F.$ )	$\epsilon.$
Calibration with benzene at 20° C.					
1.445	4.763	3.318	0.618	0.481	
1.476	4.792	3.316	0.617		
1.594	4.911	3.317	0.618		
$\epsilon$ at 25° for chlorobenzene using $C_0 = 0.481 \mu\mu F.$					
5.405	17.309	11.904	2.217		5.61
5.538	17.449	11.911	2.218		

$C_0$  and  $\epsilon$  are separately obtained from the relation  $\delta C = C_0 \cdot \epsilon - 1$  by insertion of the appropriate values.

$M_0$  and  $M_1$  are the micro-condenser readings with cell empty, and filled with liquid.

$$\delta C = (M_1 - M_0) \times 0.1862 \mu\mu F.$$

### Method of Measurement.

With cell empty and glass cover plate in position the micrometer standard condenser is read. Liquid is then pipetted into the cell and the glass plate replaced, overflow being removed with cotton wool. The condenser is adjusted to compensate for the increase in capacity and re-read. The plate is again removed, the solid dropped into the cell, and a reading taken on the condenser after compensation for further change in capacity. The cycle of operations is then reversed, *i.e.*, solid removed and cell refilled with liquid, liquid removed and cell dried out, readings on the condenser being taken at each stage. Averages of the two readings at "cell empty" and at "cell + liquid," and the single reading at "cell + liquid + solid" yield three figures which are sensibly free from small changes due to zero drift in the apparatus over the time taken to carry out one complete set of measurements.

The liquids were made up from dried samples of *n*-heptane, carbon tetrachloride, and 1 : 2-dichloro-ethane of approximate dielectric constant at 20° C. respectively, 1.97, 2.24, and 10.4. The room which contained the apparatus was kept at 20° C. throughout the experiments except for the chlorobenzene calibration, when it was maintained at 25° C.

The advantages of the above procedure are that the dielectric constants of both liquid and solid are measured in the same cell, and that the replaceable part of the condenser is wholly free from edge effects. The diamonds available for this series of measurements were  $D_{18}$  and  $D_2$ , both type 2 diamonds, separately occupying about 20 % of the volume of the cell, and  $D_{26}$ , a type 1 diamond of considerably smaller dimensions. Considerable care was taken to obtain a liquid mixture of the same dielectric constant as  $D_{18}$ , the largest diamond (for which detailed results are given), and having obtained it, no change in capacity was observed upon immersion of either  $D_{26}$  or  $D_2$ . It is thus shown that both types of diamond have the same dielectric constant.

The value obtained, 5.35, is in good agreement with that derived from the earlier direct replacement method, *viz.*, 5.26, but is probably the more correct figure as uncertainties due to air films are eliminated;  $\epsilon$  was also determined for the largest fused silica disc, which occupied about 25 % of the volume of the cell. The value obtained was 3.60. The measurements with  $D_{18}$  are set out in Table III. Detailed results for the silica are not given, but the  $\epsilon_m/\epsilon_l - \epsilon_m$  curve for this substance is shown in Fig. 4 along with that for the diamond.

TABLE III.

$M_o$ (mm.)	$M_l$ (mm.)	$M_m$ (mm.)	$M_l - M_o$ (mm.)	$M_m - M_o$ (mm.)	$\epsilon_m$	$\epsilon_l$	$\epsilon_m/\epsilon_l$
<i>Liquid No. 1.</i>							
4.295	12.425	12.857	8.130	8.562	4.31	4.15	1.040
4.300	12.435	12.863	8.135	8.563			
<i>Liquid No. 2.</i>							
4.686	13.319	13.700	8.633	9.014	4.49	4.34	1.033
4.670	13.315	13.680	8.645	9.010			
<i>Liquid No. 3.</i>							
3.358	13.858	13.976	10.500	10.618	5.11	5.06	1.009
4.121	14.607	14.727	10.486	10.606			
<i>Liquid No. 4.</i>							
4.326	15.573	15.570	11.247	11.244	5.35	5.35	1.000
4.771	16.010	16.015	11.239	11.244			
<i>Liquid No. 5.</i>							
3.904	15.804	15.677	11.900	11.773	5.56	5.60	0.992
3.760	15.646	15.549	11.886	11.789			

$M_o$ ,  $M_l$ , and  $M_m$  are respectively the micro-condenser readings with cell empty, filled with liquid, and filled with liquid + solid.

$$\epsilon = 1 + \frac{0.1862(M - M_o)}{0.481}$$

All measurements in both Parts I and II were made at a frequency of approximately one megacycle per second.

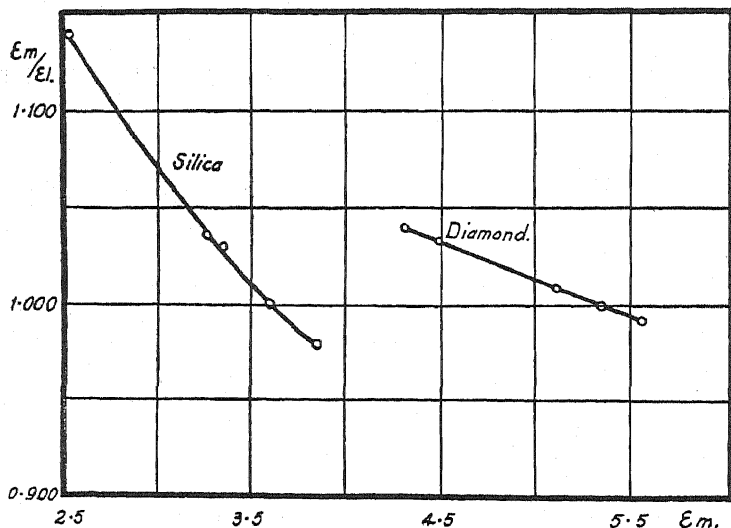


FIG. 4.

The authors wish to thank Dr. J. J. Fox, C.B., O.B.E., for facilities afforded to carry out the work, and for permission to publish.

### Summary.

The dielectric constant of diamond has been determined by two methods, (1) involving solid-air capacity changes and employing a micrometer cell of variable capacity with the diamond sandwiched between the electrodes; (2) involving solid-liquid capacity changes and employing a micro cell of fixed air capacity, with constant boundary conditions irrespective of the nature of the replaceable dielectric medium.

The capacity changes have been measured by direct compensation with a micrometer variable condenser in the tuned circuit of one oscillator of a heterodyne apparatus, the condenser readings being estimated to  $2 \times 10^{-4} \mu\text{F}$ .

The accuracy of the second method has been checked by an independent determination of the dielectric constant of chlorobenzene at  $25^\circ \text{C}$ .

The values of the dielectric constant of diamond obtained by the two methods are 5.26 and 5.35 respectively, the latter being the preferred figure.

No difference has been observed between the dielectric constants of the two types of diamond discussed by Robertson, Fox and Martin.

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## THE LATENT PHOTOGRAPHIC IMAGE: ADDITIVITY OF PART-EXPOSURES AND MICROCRYSTALLINE STATE OF SILVER HALIDE GRAINS.†

By J. C. M. BRENTANO and S. BAXTER.

*Received 30th November, 1939.*

The present paper describes, firstly, experiments on the formation of the latent photographic image in which the additive effect of part exposures is examined near the threshold and for higher densities. Their interpretation leads to an X-ray examination of the crystalline structure of photographic emulsions and to further experiments on the additive effect of exposures with different wave-lengths. These are discussed in the later part.

The original planning of the experiments was largely determined by the recent theory of Gurney and Mott<sup>1</sup> and reference may therefore be made to those features of the theory which have a particular bearing on our work.\*

† The results of this paper were presented at the Conference on Photography, held in Manchester, 3rd and 4th July, 1939, reported in *Nature*, 1939, **144**, 356.

<sup>1</sup> Gurney and Mott, *Proc. Roy. Soc., A*, 1938, **164**, 151.

\* The authors are aware that alternative interpretations of the results could be considered; e.g. they could be interpreted on the basis of secondary processes which accompany the formation of neutral halogen atoms within the grains and their migration, views developed in numerous papers. Our primary purpose was to examine how far the more recent wave-mechanical theory could account for the particular group of phenomena to which it had not been applied. It seemed thus best to use this and its development as a working hypothesis throughout. A different course, which would have led to a comparative study of a classical and of a wave-mechanical theory, was outside the scope of this work.

## 1. The Wave Mechanical Theory of Latent Image Formation.

The latent photographic image is generally assumed to consist of small specks of metallic silver in the silver halide grains of the emulsion. These specks bring about a reduction of the grains to metallic silver by the chemical action of the developer. For brevity and to distinguish such specks from the sensitivity specks, referred to later, we call such specks "active silver specks." Gurney and Mott assumed that these active silver specks result from the following process: when light is absorbed, electrons are lifted into the conduction level or conduction band of the silver halide crystals composing the grains. From the conduction band, the electrons can drop into the levels of the sensitivity specks. These sensitivity specks may consist of  $\text{Ag}_2\text{S}$  or of silver; they are assumed to pre-exist in the grains of the emulsion, prior to exposure to light. The effect of the negative charge given by the electrons to the specks, is that they attract positive silver ions. The negative charge is thus neutralised and the resulting Ag atoms form specks of metallic Ag or increase the size of silver specks already existing. As more electrons are lifted into the conduction levels of the halide crystal, this process continues and the silver specks grow. The formation of the active silver specks comprises thus two processes; one depending on the displacement of electrons, the other on the displacement of ions.

Of the more specialised picture foreseen by the theory, the following points are of particular interest for the present discussion: (1) In terms of the original theory of Gurney and Mott, an electron lifted into the conduction band of the halide crystal can leave it in two ways: it can either pass to the sensitivity specks in the way we have described; or alternatively it can fall back into the halogen atom created by its removal from a halide ion by the action of light, or into an equivalent atom formed by the removal of another electron; in which case the electron does not take part in the mechanism leading to the formation of an active silver speck. (2) The transition of electrons between the conduction levels of the halide crystal and of the sensitivity specks is similar to the transition of molecules between the liquid and gas phase of a substance, in so far as the theory assumes a finite probability for an electron to escape from the speck, while the probability that the speck may capture an electron increases with the density of the electrons in the conduction levels of the halide crystal.\* In addition, as the negative charge of the speck increases, the repelling action of this charge makes any further increase difficult. In this way, the continued condensation of electrons on the sensitivity specks depends firstly on a certain minimum density of electrons being reached in the conduction band of the crystal, and secondly on the negative charge of the specks being neutralised by positive ions.

\* At the Conference on Photography held in Manchester, 3rd and 4th July, 1939, after this paper was written, Professor Mott announced a modified form of the theory in the sense that an electron could not leave an active speck without the supply of additional energy greater than could be supplied by heat motion. Such energy supplied by infra-red radiation would account for the Herschel effect. At this conference Professor Mott also expressed his agreement with an explanation of the failure of the reciprocity law for low intensities proposed by Webb and Evans<sup>2</sup> as an alternative to the one originally proposed by Gurney and Mott; we shall refer to this later.

<sup>2</sup> Webb and Evans, *J. Opt. Soc. Am.*, 1938, 28, 431.

## 2. The Photographic Threshold.

By the photographic threshold we mean the fact that an exposure in the visible must reach a certain minimum value before the action of the developer can produce any appreciable effect. This threshold is less marked with dye-sensitized and highly sensitive emulsions than with blue sensitive emulsions of the straight type. The common feature, however, is that there is an initial range for which very little change of density with exposure takes place. From the range of practically constant density there is a more or less gradual transition to the range where, with the usual logarithmic plotting, the characteristic density-exposure curve is approximately linear.

We might interpret this threshold in the terms of the original Gurney-Mott theory as that exposure necessary before an electron concentration in the conductivity level of the crystal is reached, which is sufficient for a sustained transition of electrons to the sensitivity-specks. This would bring the phenomenon in line with the failure of the reciprocity law for low intensities, where Gurney and Mott assumed that since the electrons may return to the vacated places, their concentration in the conduction level of the halide crystal for weak illuminations remains small, so that an efficient transition of electrons to the sensitivity specks does not then take place.

From these considerations the experiments on the additive effect of part-exposures, described in the following sections, took their origin.

## 3. Experimental Arrangement.

The source of light for the exposures was a tungsten filament lamp with a blue filter transmitting the wave band from 3700 to 5200 Å. Constancy of the source was obtained by the use of a glow discharge stabiliser. As an alternative, large storage batteries, set apart for these exposures, were used, and for experiments requiring a lesser accuracy, a Solus stabiliser unit. Great attention was paid to the constancy of the source of illumination, since part of the exposures comprised time intervals of several hours. The exposure times were fixed by a rotating shutter; the intensity of illumination could be varied by varying the distance from the source. A grey wedge comprising an extreme density range of 0.2 was placed in front of the film; in this way the required exposures could be obtained within close limits. A sliding gate was used in front of the film, so that comparative exposures were taken on several strips of film. The strips ran in the direction of the gradation of the wedge, so that each intensity value was recorded in several parts of the film area. Variations of illumination as well as irregularities of coating could thus be eliminated.

Densities in the lower range were evaluated by a scatter method, described previously,<sup>3,4</sup> the particular merit of which is that by substituting the measurement of a direct effect, *viz.*, the quantity of light scattered by the silver grains, for the measurement of a difference-effect (as given by the usual absorption densitometry), higher accuracy in the range of small densities is reached. The scatter method measures essentially the number of grains, not their absorbing power. The measurements were made with a microphotometer which uses a photo-electric cell with valve amplification. Higher densities were determined by absorption photometry.

The individual exposures consisted of flashes varying in duration from 0.1" to 8", the intensities of which could be varied by adjusting the distance between source and film, a wedge being inserted, as already

<sup>3</sup> Brentano, *Z. Physik*, 1931, 70, 74.

<sup>4</sup> Brentano, Baxter and Cotton, *Phil. Mag.*, 1934, 17, 370.



indicated, so as to obtain with one exposure a range of intensity values. When comparing the densities from single and from added part-exposures, the corresponding intensities and the total exposure times were always equal.

#### 4. The Summation of Part-Exposures Separated by Varying Time Intervals.

Numerous investigations have been made concerning interrupted exposures, in the form of regularly intermittent exposures. The present work is concerned with the effect of single breaks which lead to a simpler interpretation in terms of the wave-mechanical model.\*

TABLE I.

Exposures.	Density for Contin. Exp.	Density for Interr. Exp.
110	0.0041	0.0042
127	0.0051	0.0051
137	0.0057	0.0055
145	0.0073	0.0062

In a first group of experiments conditions were chosen so that the densities were just on the rising part of the characteristic curve, they were distinctly above the fog level and rose with increasing rate. Such exposures are just past the threshold value; those for which the increase of density with exposure is still negligible or small we call sub-threshold exposures. Table I shows the total exposures in arbitrary units, the densities above the fog level for a continuous exposure and the densities obtained for two exposures separated by a time interval of 20', the first being one-third, the second two-thirds of the total. While for each table densities are inter-related, exposures on thin emulsions were used for part of the work evaluated by scatter; numerical density values have then a different meaning than when observed with normal emulsions by absorption. The emulsion used was Ilford Fine Grain Ordinary, a blue sensitive material.

It will be seen that for small exposures, the densities obtained from the superposition of the two sub-threshold exposures are substantially the same as those obtained from one continuous exposure. Exact numerical agreement between the values in the two columns is fortuitous; the order of accuracy is  $\pm 5$  per cent. The general result, that two sub-threshold exposures are additive, was confirmed for intervals separating the exposures up to 300 hours; this was also found when the part exposures were given in the ratios 1 : 1 and 2 : 1, the longer exposure in the latter case being given first. The same result was found for other types of emulsions. Ilford Line Film, Kodak Panatomic and Agfa Isopan F.

The results of similar experiments in the range of greater exposures and higher densities are represented by Fig. 1, in which we have plotted the densities resulting respectively from one continuous exposure, and from two part exposures of the same total value, the latter being given in the ratio, 1 : 2, separated by a time interval of 20'. The emulsion used was again Ilford Fine Grain Ordinary. The curves comprise results

\* For more general references on the intermittence effect, see, for instance, Kochs.<sup>5</sup> Regarding the effect of single interruptions, Long, Germann and Blair examined the superposition of part exposures for Azo paper. Brush, Norman and Albersheim<sup>6</sup> observed the change of the effect of pre-exposure with time; Brush found a decrease for very small pre-exposures and additivity for larger exposures; Norman found a decrease of the sensitizing action for intervals from 3-20 hours, while Albersheim examined the change on the modulation of a sound track.

<sup>5</sup> Kochs, *Z. wiss. Phot.*, 1937, **36**, 97.

<sup>6</sup> Long, Germann and Blair, *J. Opt. Soc. Am.*, 1935, **25**, 382; Brush, *Physic. Rev.*, 1910, **31**, 241; Norman, *J. Opt. Soc. Am.*, 1936, **26**, 407; Albersheim, *J. Soc. Motion Picture Eng.*, 1939, **32**, 73.

obtained from several plates, and to interlink these results, a curve has been traced from a limited number of density steps which were all recorded on one plate and marked by  $\odot$ : on this curve the relative densities for

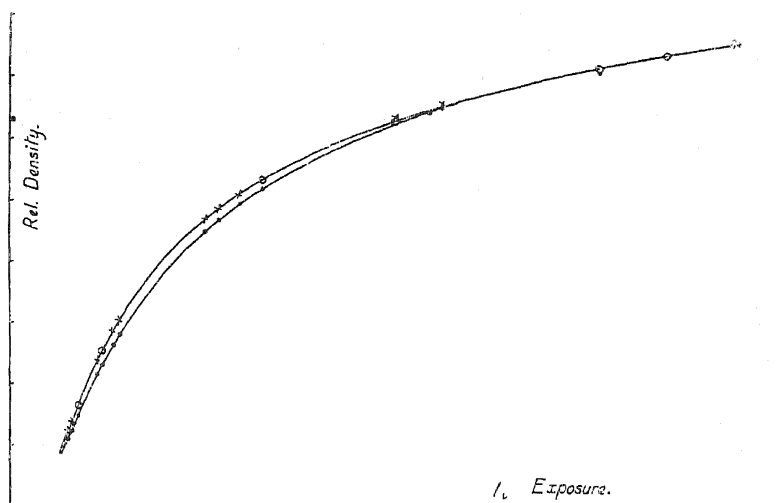


FIG. 1.

single exposures and for exposures given in parts are marked by a cross and a dot respectively.

In the range of greater exposures, the density obtained from two part exposures is less than that obtained from the equivalent exposure given without interruption. The deficiency is greatest in the range of medium densities where the decrease in density is of the order of 20 per cent.; it falls off for small and for high densities.

The effect of the interruption in reducing the density attains approximately its full value for an interval of 20' between the part exposures. This is shown in Table II, where the densities obtained for medium exposures are shown for time intervals of various lengths. The emulsion used was again Ilford Fine Grain Ordinary.

TABLE II.

Interval between Exposures.	Density for Contin. Exp.	Density for Interr. Exp.	Difference.
2'	0.234	0.237	- 0.003
5'	0.246	0.234	+ 0.012
20'	0.278	0.254	0.024
60'	0.260	0.239	0.021
360'	0.244	0.222	0.022

The small increase for the interval of 2' has no real significance; it falls within the limits of error. The result of a great number of observations is that no change was observable for intervals less than 2' 30", for 5' it was very distinct, for 15' it had almost acquired its full value. From there on only a very slow change with density took place. These times vary greatly with different emulsions.\*

Experiments, in which the ratios between the first and second exposure were 1 : 1 and 2 : 1—the longer exposure in this case being given first—gave qualitatively similar results to those shown in Fig. 1.

\* We must consider how far the deficiency observed with interrupted exposures is possibly affected by the fact that the time interval between exposure and development is necessarily lengthened for part of the exposures in those experiments where the exposure is interrupted. Various results are recorded on

Experiments with other emulsions, Ilford Line Film which is blue sensitive, Kodak Panatomic and Agfa Isopan F, which are panchromatic, also gave a deficiency of density for interrupted exposures. The average grain size of Ilford Fine Grain Ordinary is approximately 2.5 times larger than that of Ilford Line Film; the deficiency resulting from interrupted exposures was observed after a shorter break for the emulsion with finer grain. Similarly, with the two panchromatic emulsions, the deficiency appeared after a shorter interval with Kodak Panatomic, whose average grain size was approximately half that of Isopan F. No systematic survey of these emulsions, however, was made.

Experiments with several interruptions gave results qualitatively similar to those with a single break. Under the conditions in which these gave a decrease in density, such a decrease was larger when several interruptions occurred.

TABLE III.

Density for Contin. Exp.	Density for Interr. Exp.	Difference.	Difference (%)
0.149	0.084	0.065	43
0.170	0.089	0.081	47
0.209	0.117	0.092	44
0.247	0.142	0.105	43

As an example, interruptions of 20' were interposed between six part exposures, each being one-tenth of the total, followed by the remainder of the exposure, given without a break; these were compared with exposures of the same total value given without interruption. For small densities—the six part exposures then falling within the sub-threshold range—no decrease in density was observed; this agrees with corresponding experiments with a single break. For higher densities, losses of density were observed (Table III) of the order of 43 %-47 %, considerably greater than those observed with one single interruption, when the greatest density loss was 20 per cent.

Table IV shows the comparative effect of interruptions in the early and in the later part of the exposure; in (A) the first four-tenths of the exposure were given in four separate parts at intervals of 20', and the remainder in one unit. In the experiments recorded in (B), the early part of the exposure was given without a break, while the last four-tenths of the exposure were given in separate parts at intervals of 20'. Again, it will

the effect of the time between exposure and development on density.<sup>7</sup> In general, it is found that such an effect becomes noticeable only after longer time intervals than those used in our experiments and that it would tend to produce a density change opposite to that observed by us. Tests which we made under the conditions of our experiments, gave the results shown in the accompanying table, where the three vertical columns show the densities obtained. The film was equally exposed for each of the three values given in one column, while the time between exposure and beginning of development varied as indicated. The film used was Ilford Fine Grain Ordinary.

It will be seen that the values for each column agree within 1 per cent.; a 20' period between exposure and development should thus not appreciably affect the results. This interval was used in most of our experiments on interrupted exposures.

Time between Exposure and Development.	Densities.		
25"	0.512	0.530	0.608
20'	0.515	0.532	0.605
40'	0.517	0.534	0.602

<sup>7</sup> Hylan and Blair, *J. Opt. Soc. Am.*, 1935, **25**, 246; Brush, *Physic. Rev.*, 1910, **31**, 241; Carroll, *J. Physic. Chem.*, 1925, **29**, 693; Jausseran, *Sci. Ind. Phot.*, 1929, **9**, 85, 167; Narbutt, *Z. wiss. Phot.*, 1932, **31**, 146; Blair and Leighton, *J. Physic. Chem.*, 1932, **36**, 1649; Bullock, *Sci. Ind. Phot.*, 1932 (2), **3**, 201; 1933 (2), **4**, 33.

be seen that for the smallest densities, no appreciable or only small density losses are produced by the repeated breaks at the beginning or the end of the exposures. For somewhat greater densities, deficiencies of about 30 % are observed, and are appreciably the same, whether the interruptions take place during the early or later stages. For higher densities, the deficiencies become small, when the interruptions are given in the later part of the exposures; they still remain high—of the order of 20 %—when the breaks occur at the beginning.

The following experiments acquire a special significance with regard to a later discussion: Three breaks of 20' each were given after four-, five-, and six-tenths of the exposure and the densities were compared with those obtained from an uninterrupted exposure. The average deficiency observed for a group of measurements covering the density range from 0.022 to 0.055 was 27.8 % of the density. An experiment was made covering the same density range, but with one break of 60' after the first half of the exposure; \* the average deficiency was then only 15.5 %. In a third experiment, with a single break after the first half of the exposure, but of 20' duration only, the average deficiency was also 15.5 %. The total exposures were the same for the three experiments and were so small, that the part-exposures falling between the two consecutive breaks in the first experiment were of the order of the threshold. It is seen that the deficiency produced by a single break is the same whether it lasts for 20' or for 60', whilst repeated breaks produce a considerably larger deficiency than one single break of the same total duration.

TABLE IV.

Density for Contin. Exp.	Density for Interr. Exp.	Difference.	Difference (%).
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**A. First 4/10 of Exposure Interrupted.****Smaller Densities :**

0.0088	0.0084	+ 0.0004	+ 4.5
0.0108	0.0112	- 0.0004	- 3.7
0.0120	0.0112	+ 0.0008	+ 6.5
0.0128	0.0111	0.0017	13
0.0176	0.0132	0.0044	25
0.0276	0.0183	0.0093	33
0.0390	0.0267	0.0123	32

**Higher Densities :**

0.237	0.167	0.070	30
0.323	0.237	0.086	27
0.410	0.301	0.109	27
0.546	0.432	0.114	21

**B. Last 4/10 of Exposure Interrupted.****Smaller Densities :**

0.0066	0.0068	- 0.0002	- 3.0
0.0074	0.0072	+ 0.0002	+ 2.7
0.0082	0.0080	0.0002	2.5
0.0096	0.0089	0.0007	7
0.0120	0.0104	0.0016	13
0.0140	0.0098	0.0042	29
0.0199	0.0148	0.0051	26
0.0304	0.0216	0.0088	30

**Higher Densities :**

0.214	0.190	0.024	11
0.301	0.285	0.016	5
0.374	0.362	0.012	3
0.477	0.461	0.016	3

## 5. Discussion of the Experiments on the Summation of Part Exposures Separated by Time Intervals.

The essential result for small densities is that in the neighbourhood of the threshold part exposures are additive, even when separated by

\* The interruptions were placed in the middle part of the exposure because in one particular interpretation specks broken up with the interruption may be rebuilt during the final exposure. This process, which is difficult to allow for quantitatively, is small so long as the final exposure is not longer than the first.

long time intervals, and that the effect of the initial exposure—which then falls within the sub-threshold range—possesses a considerable degree of stability. Considered on the tentative model of the threshold indicated in Section (2), it would be expected that the initial stages of an exposure should serve primarily to build up the electron concentration in the conduction level for an efficient transition of electrons to the sensitivity specks to take place. If an exposure were interrupted at this point the electrons should fall back to their original positions in the lattice of the halide crystal without contributing, except to a limited extent, to the formation of active specks. A second exposure after a sufficient time interval should find the grains substantially in the same state as if no previous exposure had been given. For sufficiently long time intervals between the part exposures there should thus be a decrease of density and, in fact, the experiments were originally undertaken with the object of thus measuring the average time of retention of electrons in the conduction level. This time should be of the order of one hour,\* considerably shorter than the time-interval used in some of our experiments. Since, for the production of small densities sub-threshold exposures are additive, the threshold cannot be accounted for by an accumulation of electrons in the conduction level. It seems thus improbable that a process of this kind should play any large part in the phenomena with which we are here concerned.

For larger exposures a deficiency in density was observed, increasing with the time interval separating the part exposures up to a certain value, which for one particular emulsion was of the order of 20'. This would be in reasonable agreement with the time which electrons may be expected to require to leave the conduction level of the halide crystal and to revert to their original positions, so that we could interpret the phenomena on the basis of the model we have just discussed, except for the fact that the same model would not account for the phenomena observed for very low densities.

On the assumption that the same model should apply to the phenomena near the threshold and at higher densities we can here also refer to the effect of low temperatures discussed in Section (6), where it is found that the density decrease or regression disappears at temperatures below  $-90^{\circ}\text{C}$ . The falling back of electrons from the conduction level into their original positions in the halide crystal should take place also at the lower temperatures. It will thus be seen that this process cannot, at any rate alone, account for the phenomena where a regression is observed.

Another way of interpreting the experiments is to assume a general instability of small silver specks, leading to the break-up and loss of specks during the early stages of their growth. Such instability, due to thermal energy, has been suggested by Webb and Evans,<sup>3</sup> in order to account for the low intensity reciprocity law failure which they and Weinland<sup>8</sup> observed. They assumed the probability of such a thermal disintegration to be higher for a small than for a large speck and "that the stability of the latent image speck does depend upon its size, and

\* In the original Gurney-Mott theory which forms the basis of this discussion the time for electrons to be retained in the conduction level can be estimated from the discussion given in one of the papers<sup>1</sup> and more directly from the time over which an exposure must be extended in order to show a marked low-intensity deviation from reciprocity law.

<sup>8</sup> Weinland, *J. Opt. Soc., A.*, 1928, **16**, 295.

when it has reached about half its final size, then it is perfectly stable and does not disintegrate under temperature motion" (p. 434). Applying this model to our experiments, we might interpret the regression as due to the loss of those specks which are unstable. The rate of disintegration for some group of specks, as determined by the fact that the model accounts for the low intensity reciprocity law failure, could well agree in order of magnitude with the regression period for an interrupted exposure. One point to be considered, however, is that for the smallest specks we should expect a very rapid disintegration, decreasing gradually for those specks near the size at which they are stable, which initially would decay very slowly. There should thus be a very marked regression for very short interruptions with a gradual protracted increase for longer periods; this does not correspond with what we have observed.

If we compare the effect of repeated breaks with that of single interruptions (see the group of experiments discussed at the end of Section (4)), it is noted that repeated interruptions, separated by only small intermediate exposures, give a regression considerably greater than that produced by one single interruption of the same total duration. In terms of a general break-up of small specks this implies a very short range of instability, since otherwise with three and with one interruption essentially the same specks should have been affected. From our experiments, the range of instability of the specks can be expressed by the intermediate exposure between successive interruptions necessary for the additional density loss to acquire its full value; for larger intermediate exposures the number of additional new specks is balanced by a corresponding number of specks lost. The experiments show then that this range is very small. It is then reasonable to place this range of instability in the early stages of the speck's growth, so that these specks which can be lost with an interruption of the exposure are essentially those which originated in the small exposure range immediately preceding the break. We have seen in Section (4) that one single interruption can produce a density loss of 20 %, which in the range of medium exposures represents the loss of a considerable number of specks, and that the interruption can take place at various stages of the exposure, so that each stage at which an interruption is effective in producing a considerable density loss should be preceded by a narrow range in which a large number of specks originate. It is difficult to co-ordinate this narrow range of instability with the fact that an interruption, whether in the early or in the later part of the exposure, can produce a marked density loss. This difficulty is accentuated if we assume that the majority of active specks result from a cumulative process\* involving many quanta, when on statistical grounds the initial stages of their growth should mostly take place during the early part of an exposure. An interruption outside this early part should not then be effective in producing a regression.

We can arrive at a formal interpretation of the results, in which a gradual formation of active silver specks by a cumulative action is actually demanded, if we assume that the interruption of the exposure produces a certain regression or "stepping back," in the sense that at the

\* While the older theories largely assumed such a cumulative action, some recent authors, *e.g.* Silverstein and Trivelli,<sup>9</sup> favour the view that only one or two quanta need be received by a sensitive speck in order to produce an active development centre. We shall revert to this point in a later section.

<sup>9</sup> Silverstein and Trivelli, *J. Opt. Soc., A.*, 1938, 28, 441.

beginning of the second exposure the specks are no longer in the state they had reached when the first exposure was interrupted; in this way, the second exposure could only contribute to the further growth of the silver specks after a certain amount of leeway, as it were, had been made good. Such an effect should take place for the early stages of the growth of the specks, and should lead, not to their complete disappearance, but merely to a limited regression. We can then understand that the density loss increases with the number of breaks; furthermore, in the case of exposures not exceeding the limit within which the particles are susceptible to regression, a later break may have a similar effect to an interruption in the earlier part of the exposure. By assuming that specks which have already attained a considerable size, or which result from a process of very gradual growth, are not subjected to such a regression, we can understand that an interruption in the later part of a large exposure is less effective. The regression should be most noticeable at those densities at which the number of active silver specks increases most rapidly with the exposure and when the interruption takes place within the critical stage of their growth. This accords with Fig. 1. The density loss falls off for small and for very high densities, because (1) when the number of developable grains increases slowly with exposure, a stepping back by a small amount—equivalent to a certain loss of exposure time—affects the formation of few active specks only; (2) in both the extreme regions an interruption only affects specks which are already large.

In an alternative formal interpretation, we avoid the difficulties found with a general break-up and loss of small specks by substituting a more specialised process which provides that: (1) at any stage of the exposure only a limited number of specks can break up and for these specks the rate of disintegration is high, while the remainder of the specks are stable; and (2) specks liable to break up are found throughout the greater part of the exposure range. Such a mechanism gives results formally almost equivalent to those of the stepping back action.

We may consider whether a physical significance could be given to one or the other of these models. We can account for the "stepping back action" if it is possible to assume that electrons and ions on joining a small speck do not at once take up their fully consolidated positions and that, say, the last electron may be unstable and in a position to leave the speck with thermal energy. As to the alternative, a breaking-up process satisfying the two conditions last mentioned could be found in a two-quantum process, when specks with but one electron would be definitely unstable and would possibly lose and regain this electron repeatedly. Such a process would also avoid the crowding of the initial stages of the formation of specks into the early part of the exposure, which results from a cumulative process involving many quanta.

## 6. The Effect of Low Temperatures on the Regression.

In these experiments the photographic material was kept at a low temperature during the interval between the part exposures. Cooling took place in less than 40" and the period of warming was approximately 50"; the total time during which the emulsion was not at low temperature was thus less than the time required for any appreciable regression to take place. Experiments were carried out at liquid air temperature and at somewhat higher temperatures up to  $-90^{\circ}\text{C}$ , and no appreciable regres-

sion could be observed. In one typical experiment, the interval between the first third of the exposure and the remaining two-thirds was increased to 6 hours, while the temperature was maintained between  $-90^{\circ}\text{C.}$  and  $-79^{\circ}\text{C.}$ ; the densities of the interrupted exposure agreed with those of a continuous exposure within 2 %, the limits of error.

The loss of electrons from the conduction level of the halide crystal by direct return to their original positions, considered in Section (2) with regard to the threshold, should not show such a change with temperature. The experiments prove thus that this process by itself could not account for the regression effect, but that regression must depend on processes involving the mobility of ions or the supply of thermal energy for the escape of electrons.

### 7. The Effect of Infra-Red Radiation on the Regression.

In these experiments we flooded the photographic material with infra-red radiation during the interval between the part exposures. Two sources were used corresponding to emitters at  $590^{\circ}\text{K.}$  and  $540^{\circ}\text{K.}$  With the source of higher temperature ( $590^{\circ}\text{K.}$ ) a distinct Herschel effect took place, which could be observed from comparing density-marks obtained with single exposures given before and after the irradiation with infra-red. Within the limits of accuracy the irradiation between the part exposures produced, however, no increase of the regression, after making allowance for the normal Herschel effect on the fully formed developing centres. Corresponding exposures under identical conditions but with the source at  $540^{\circ}\text{K.}$  gave no observable normal Herschel effect and produced also no increase of the regression as compared with experiments where between the part exposures no flooding with infra-red had taken place.

### 8. The Cumulative Effect and the Threshold.

The tentative interpretation of the threshold discussed in Section (2) is essentially a specialised way of interpreting it as a statistical effect. The problem has a wider significance in view of the point raised in Section (5) as to whether the formation of active specks results from a process involving only two or a larger number of quanta. The following sections refer to this question.

If an active silver speck is produced by the absorption of a single light quantum, then for the early stages of an exposure proportionality should exist between the exposure and the number of active silver specks produced. This is found for exposures with X-rays of high frequency, when one X-ray quantum supplies the energy necessary for the formation of one speck, the absorption taking place by way of the formation of secondaries. Not only is no threshold then observed, but proportionality exists between exposure and the increase in the number of developable grains. Accurate measurements for very small densities were made on this point, using the scatter method for determining the number of developed grains.

When, on the other hand, the formation of an active silver speck requires the absorption of a large number  $n$  of light quanta, then it is improbable that these  $n$  quanta will be absorbed within the volume of the grain or of a crystallite forming part of a grain in the course of an exposure smaller than the average exposure required for the absorption of  $n$  quanta within this volume; and it becomes the more improbable the more the exposure in terms of this average value is small and the number  $n$  is great. If all grains were alike and each required the absorption of the same number of quanta, then the probable fluctuation in the exposures required for producing a developable grain should extend through a range of  $1/\sqrt{n}$  of the exposure. With increasing  $n$  it becomes extremely improbable that these  $n$  quanta should be absorbed during an exposure considerably shorter than the average exposure required. With a large value  $n$ , a well-defined threshold range should thus be observed.



Fig. 2 shows a characteristic curve for Ilford Fine Grain Ordinary giving the density against the logarithm of exposure,\* and also curves giving the distribution of the probability for the absorption of  $n$  quanta for  $n = 5$  and  $n = 10$ , the scale being again logarithmic and the abscissæ being so adjusted that the probable absorption of 5 and 10 respectively are made to coincide with the middle of the steep rise of the characteristic

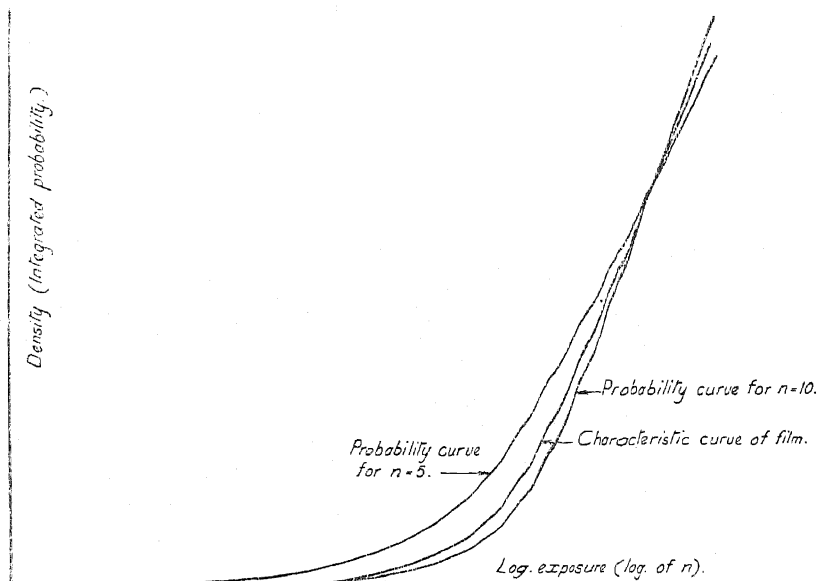


FIG. 2.

curve. It will be seen that the run of the characteristic curve falls somewhat between that of the probability distribution curve for  $n = 10$  and  $n = 5$ . Nothing more than a rough qualitative correspondence can be expected, since different values of  $n$  apply to different grains, tending to smooth out the rise of the characteristic curve. The comparison of the calculated curves would suggest that the average value of  $n$  should be of the order of 10.

\* *Added in Proof*: The same statistical method is discussed in two papers by Webb,<sup>10</sup> which appeared after the Manchester Conference. The first may also be referred to for earlier literature. In the second paper Webb shows by a detailed analysis that with appropriate assumptions  $H$  and  $D$  curves can be accurately accounted for on a statistical basis. Our aim was essentially to account for the threshold, and to use the  $H$  and  $D$  curve for finding whether the formation of active specks comprises two or more stages. Nothing more than a very approximative answer appears justified, so long as the various parameters (size and sensitivity distribution, absorption in the emulsion), are not actually known from data which should be independent of this particular interpretation. To reduce this uncertainty we considered in the first place the foot of the  $H$  and  $D$  curve (see the account of the Manchester Conference in *Nature*), where the effect of absorption is less disturbing, while Webb, in his analysis, considers the general steepness. We do not, however, suggest that differences in findings should be attributed to differences of method, but rather to the different character of the emulsions; we used an emulsion with steep gradation. To discuss the theory of latent image formation, it seemed best to apply it to the greatest variety of data obtained for one and the same photographic material: one of simple and uniform type was chosen.

<sup>10</sup> Webb, *J. Opt. Soc. Am.*, 1939, 29, 309 and 314:

## 9. X-Ray Examination of the Microcrystalline State of the Grains of Photographic Emulsions.

We examined the relation between sensitivity and the state of crystalline subdivision of the grains by determining the average size of the crystallites composing the grains of various emulsions. The experimental details regarding these measurements will be reported in a separate paper. The general finding, which is of interest here, was that emulsions with coarse grains gave broader X-ray lines indicating that the crystallites composing the grains were either smaller or more highly deformed. This was found in particular with regard to coarse grain emulsions of high sensitivity, the grains of the more sensitive emulsions showing a state of greater distortion or a higher degree of sub-division.

Apart from measurements made on commercial emulsions experiments were made on the effect of sensitizers upon the condition of the crystallites. Two particular instances may be quoted: when  $\text{Ag}_2\text{S}$  was introduced in such a way as to act as an efficient sensitizer the X-ray lines were broader than those from a similar emulsion of the same average grain size of pure  $\text{AgBr}$ , and broader also than those of a similar emulsion containing  $\text{Ag}_2\text{S}$  but introduced in such a way as not to act as a sensitizing agent. When an emulsion was exposed to the action of mercury vapour, under such conditions as to act as a sensitizer then with the increase of sensitivity also a decrease in the regularity of the crystalline state of the grains could be observed. These experiments do not establish that the increase of sensitivity produced by the action of a sensitizer is caused by the deterioration of the microcrystalline structure; both phenomena may go parallel without one being the cause of the other. We have, in fact, some evidence that in certain cases a specific sensitizing action can take place with but little or no deterioration of the lattice. What can safely be said is that the coarse grains of sensitive emulsions are largely subdivided or deformed.

The breaking up of grains into smaller units and the formation of more internal boundaries may actually affect the sensitivity in different ways. It might decrease the sensitivity in so far as active silver specks can act as developing centres only when situated near the external surfaces of the grain, while internal boundaries may give the opportunity for electrons to collect and specks to form in the interior in places which are not accessible to the developer. On the other hand, it might increase the sensitivity in so far as the subdivision enhances locally favourable conditions to have full effect; this would be in accordance with the theory of Gurney and Mott.\*

## 10. The Summation of Exposures with Different Wave-lengths.

An alternative interpretation of the threshold could arise if during the early stages of the exposure some other process took place preceding the formation of active specks. Such a process could be imagined to consist in the trapping of electrons at some intermediate levels. In regard to the

\* According to this theory, as indicated in section (2), large  $n$  numbers might be associated with large grains. The discussion in section (8) would then suggest that the threshold value should be particularly great, while it is generally found that for coarse grain emulsions the initial sensitivity is high and the threshold small. The X-ray examination shows that such grains are actually subdivided into small crystallites and this would account for the  $n$  numbers being small. It should not be overlooked that another reason for the high sensitivity of coarse grains may result from the inequality of the specks: a limited number of specks with enhanced sensitivity would provide a larger contribution to the resulting density when the grains are large, since each active speck entails the development of a whole grain.

existence of such electron traps, the following experiments were made : \* Two exposures with different wave-lengths were given in succession. It could be expected that if a first exposure with a short wave-length had brought electrons into some intermediate levels, a subsequent exposure with longer wave-lengths, so long as not to be very efficient in lifting electrons from their original places into the conduction band, would be more effective in producing active silver specks than when the exposures were given in the reversed order ; the opposite effect would arise with electrons trapped very firmly. A wave-band in the blue and in the yellow were used (the yellow one being chosen so that a prolonged exposure would still yield a high density) and the intensities were so adjusted that for the single exposures equal densities were obtained for equal exposure times. If for each of the two wave-lengths the action of light were the same, the deviation from the reciprocity law should be equal in each case. It was then found that for low densities the resulting density was independent of the sequence of the exposures (and this applies also when the added effect of the two exposures just exceeded the threshold), but that for high densities there was a distinct difference suggesting a small amount of trapping at deep levels. Webb,<sup>11</sup> who made an extensive examination of the additive effect of exposure with two wave-lengths, did not observe this effect. It is very small and not noticeable outside the range of high densities, and was possibly not observed in earlier work for this reason.

## 11. Discussion of the Experiments of Sections 6 to 10.

In Section 5 we have summarised our results by reference to the two alternative working hypotheses, *viz.*, that the regression may be due to the loss of specific electrons, or to a "specialised" break-up which could be accounted for by a two-quantum process.

The fact that the regression disappears on lowering the temperature shows that it must depend on some phenomenon requiring thermal energy, this could apply to either the loss by the speck of specific loosely held electrons or the break-up of small specks.

On this latter view, flooding with infra-red should have increased the regression, in view particularly of Mott's interpretation of the Herschel effect as the breaking up of fully formed active silver specks. In analogy a somewhat smaller energy should considerably enhance the disintegration of smaller specks, for which according to the model of Webb and Evans the chance for disintegration should gradually increase with decreasing size of the specks. If, on the other hand, the regression consisted in the loss of specific incompletely consolidated electrons or ions, leaving the speck by thermal energy alone, flooding with long wave infra-red should not alter the number of electrons lost. This view would thus conform with the results of the experiments.

In this model, which foresees that some specific electrons are unstable, the time during which the regression increases can then be taken as the average time for such losses of electrons to occur through their thermal energy. In a modified interpretation we may assume that the incompletely consolidated electrons are much less stable than is

\* The experiments on the additive effect of exposures to two different wave-lengths, here reported, were first undertaken in the range of small densities by one of us (J. C. M. B.) in collaboration with W. J. Meredith and formed part of the thesis (1936) of the latter. For the later experiments in the range of higher densities one of the writers (J. C. M. B.) had the collaboration of J. B. Sharples and J. R. Whitehead. Recently Berg reported in these *Transactions* (1939, 35, 445), on analogous experiments in the range of low temperatures.

<sup>11</sup> Webb, *Phot. J.*, 1935, 76, 78.

indicated by the regression period, but that they are replaced on the specks so long as a sufficient electron density is maintained in the conduction level. The maintenance of such a state and the regression period would then essentially be determined by the time during which the electrons remain in the conduction level before falling back into their original positions in the crystal lattice. To account for the disappearance of the regression at lower temperature we then assume that at low temperatures the electrons do not possess the necessary energy for leaving the speck. We do not wish to attach to one or the other version any other significance than that of correlating the experiments. Regarding the alternative model, we have indicated the conditions under which a break-up and loss of small specks could account for them. These could be satisfied by a break-up essentially restricted to definite groups (the initial stages). Repeated transitions of electrons between speck and conduction band, of the kind indicated in the second version of the model just discussed, could then determine a regression period. The forming of an appreciable number of active specks, right from the initial stages, becomes possible if specks were made in only two or few stages. The following discussion leads to this point:—

Section (8) which is primarily concerned with the threshold, shows that it can be accounted for on a statistical basis, and that the assumption of a cumulative effect for the formation of active silver specks (which also forms the basis of the theory of Gurney and Mott) is sufficient to account for the threshold and the early rise of the density-exposure curve. On this statistical interpretation, for a blue sensitive material, the majority of active specks should result from a gradual growth involving more than two, and on the average approximately ten quanta. X-ray determinations show that, in general, increased sensitivity goes parallel with a more highly deformed or more highly subdivided microcrystalline structure. This may be due to the fact that, with a division of the grain in smaller units, locally favourable conditions are given greater weight. It may also be due to the formation of intermediate electron levels at which electrons can be trapped, and which can have the effect of increasing the sensitivity. The initial accumulation of electrons in such traps could provide an alternative interpretation for the threshold which should then not necessarily be considered as resulting from a cumulative effect. The experiments on the summation of part exposures with different wave-lengths showed differences which can be interpreted as trapping, although only for high densities.\* While this is of interest, it fails to account for the phenomena at low densities and at the threshold.

With regard to the formation of active specks and the particular assumption, that they result from a two-quantum process and that breaking up occurs while only one quantum has been received, the fact that, on a statistical basis, the threshold can be accounted for by a cumulative process involving a greater number of steps and not by a two-quantum process does in itself not disprove such a process, so long as the threshold can be accounted for in an alternative way. The one here considered is that electron traps may exist at intermediate levels; the experiments

\* In referring to the results in this way, we do not exclude that other reasons may account for any change of the densities with the order of the exposures; but the fact that no such change was observed in the range of low densities justifies the interpretation in the sense that in the initial stages no trapping occurs.

do not confirm the existence of such traps for exposure near the threshold. This does not preclude that the threshold may be accounted for on a different basis.

## 12. Conclusions.

The examination of the photographic action of part exposures showed that part exposures are additive even when separated by time intervals of 300 hours, when their summation produces a density of low value indicating a marked stability of the effect of sub-threshold exposures. In the range of higher densities a deficiency or regression of density is observed; for one particular emulsion this becomes noticeable when the interruption exceeds 3' and attains a finite value for an interval of 20'. This regression is greatest in the range where the density increases most rapidly with exposure; it falls off in the range of small and of high densities. It increases with the number of interruptions. No regression is observed when the photographic material is maintained at a temperature below  $-90^{\circ}$  C. The regression is not modified by flooding the photographic material with infra-red radiation.

An X-ray examination of the microcrystalline structure of the grains showed that in general the grains of more sensitive emulsions consist of more deformed or more highly subdivided crystallites.

Experiments on the summation of exposures to light of different wave-lengths showed that for large exposures the densities depend on the order in which they are given. For small exposures no such effect was observed.

The various results with regard to the threshold and to the regression effect can be co-ordinated by assuming that for a blue sensitive material the large majority of active specks results from a process of gradual growth involving approximately ten steps, and that the interruption of an exposure is followed by the loss of a limited number of electrons, either from specks which are small or from specks on which they are held in unstable positions. An alternative assumption of a break-up of small specks, limited to the early stages of a process of growth involving two or few steps only, is contingent to finding that the threshold can be accounted for without recurring to a multi-quantum process.

## Summary.

Experiments on the formation of the latent photographic image, in particular the threshold and a regression or deficiency observed in the addition of part-exposures, are described.

The dependence of this regression on density, on the length and number of interruptions, and the manner in which it is affected by cooling and by flooding with infra-red are examined.

Subsidiary experiments comprise a statistical discussion of the threshold, an X-ray examination of the micro-crystalline state of the grains of photographic emulsions and experiments on the super-position of radiations with different wave-lengths.

The results are discussed with regard to possible interpretations derived from a wave-mechanical model.

The authors wish to express their thanks to Professor Mott, Professor Peierls and Dr. Gurney for discussions and suggestions received during the course of this work. They are also grateful to Professor Mott for the privilege of perusing MSS. of his papers and receiving first-hand information on the development of the theory and to Dr. Berg for various valuable indications and for drawing their attention to papers which were not easily accessible.

They are also greatly indebted to Dr. Bloch and to Messrs. Ilford Ltd. for having provided a number of special photographic materials which were most valuable in carrying out this work.

One of us (S. B.), is indebted to the Department of Scientific and Industrial Research for a grant which enabled him to devote his time to the investigations described.

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## MONOLAYERS OF COMPOUNDS WITH BRANCHED HYDROCARBON CHAINS. I. DI-SUBSTITUTED ACETIC ACIDS.

BY EINAR STENHAGEN.\*

Received 15th February, 1940.

The properties of insoluble monolayers of compounds with normal hydrocarbon chains and different polar groups are well known. This knowledge is largely due to the systematic researches of Adam and his associates.<sup>1</sup> No work has been carried out, however, on compounds with branched hydrocarbon chains. Carboxylic acids with branched chains are important from the biological point of view. Adams and collaborators<sup>2</sup> have shown that certain acids of this type have a bactericidal action against certain bacteria, and other investigators have shown that branched acids are normal constituents of several bacteria. The most remarkable discovery is perhaps that one acid of this type, isolated from the tubercle bacillus by Anderson and Chargaff,<sup>3</sup> and called the phthiolic acid, is responsible for the tissue reaction characteristic of tuberculosis.<sup>4</sup>

A study of the surface film properties of different branched chain acids may, in favourable cases, give valuable information as to the structure of naturally occurring acids, by comparing the data obtained with the acid of unknown structure with those obtained with acids of known constitution. Furthermore, by the technique developed by Schulman and Rideal and associates<sup>5</sup> it is possible to study their interaction with other chemical compounds in surface films.

\* Rockefeller Foundation Fellow, 1938-39.

<sup>1</sup> N. K. Adam, *The Physics and Chemistry of Surfaces*, 2nd edition, Oxford, 1938.

<sup>2</sup> (a) R. Adams, W. M. Stanley and H. A. Stearns, *J. Amer. Chem. Soc.*, 1928, 50, 1475. (b) G. R. Yoke and R. Adams, *ibid.*, 1928, 50, 1503. (c) J. A. Arvin and R. Adams, *ibid.*, 1928, 50, 1983. (d) L. A. Davies and R. Adams, *ibid.*, 1928, 50, 2297; (e) W. M. Stanley, M. S. Jay and R. Adams, *ibid.*, 1929, 51, 1261. (f) S. G. Ford and R. Adams, *ibid.*, 1930, 52, 1259. (g) B. F. Armendt and R. Adams, *ibid.*, 1930, 52, 1289. (h) C. M. Greer and R. Adams, *ibid.*, 1930, 52, 2540.

<sup>3</sup> (a) R. J. Anderson and E. Chargaff, *J. Biol. Chem.*, 1929-30, 85, 77. (b) R. J. Anderson, *ibid.*, 1932, 97, 639.

<sup>4</sup> F. Sabin, *Physiol. Rev.*, 1932, 12, 141.

<sup>5</sup> (a) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., B*, 1937, 122, 29 and 46. (b) J. H. Schulman and E. Stenhagen, *ibid.*, 1938, 126, 356. (c) E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, 1939, 35, 716.

### Technique.

The measurements were carried out using a Langmuir-Adam trough in the usual manner. The surface potential was measured by means of a polonium electrode and a Lindemann electrometer, as described by Schulman and Rideal.<sup>6</sup> A trough of Pyrex glass and a mica boom were employed, in order to avoid heavy metal ions. The water used was free from copper ions and the chemicals were of "Analar" grade. The material to be spread was dissolved in redistilled petrol ether (B.D.H., Bp. 60-80° C.) and spread by means of an "Aglā" micrometer syringe.

The torsion wire balance was sensitive to 0.1 dynes. Due to the relatively low sensitivity of the apparatus used, the investigation of the acids at very low surface pressures was left for future work.

At least two separate sets of measurements were carried out with freshly prepared petrol ether solutions, and it is considered that the *F-A* curves are accurate within 2-4 per cent. The nature of several of the acids used does not allow extreme accuracy to be obtained. The time interval between different points on the *F-A* curves is about 45 sec.; with different rates of compression slightly different areas will be found, in general, slightly smaller areas will be obtained on very slow compression. The difference will be significant only in cases where the acids collapse readily at higher pressures, in such cases the *F-A* curves are dotted.

The surface potentials were read to the nearest millivolt, and each point on the curves is the mean of measurements on three different points on the surface. Above 1 dyne pressure, the potentials were uniform to 4 mv.

The measurements were carried out at a temperature of  $18 \pm 1^\circ \text{C}$ .

In order to simplify the figures and conserve space, the acids are characterised only by the number of carbon atoms in the two branches, if these have normal chains. The 2:10 acid is thus ethyl-decyl-acetic acid, and the 0:15 acid the straight chain margaric acid.

### Material Used.

This work was made possible by the generosity of Professor Roger Adams, University of Illinois, who placed a large number of synthetic acids at the author's disposal. Details of the synthesis, purification and physical constants of the various acids will be found in the original papers by Adams and collaborators.<sup>2</sup>

In addition, the  $\text{C}_{26}$  acids and the ethyl-tetradecyl-acetic acid were obtained from Dr. E. Chargaff, New York,<sup>7</sup> the margaric acid from Professor F. Francis, Bristol, and the di-octadecyl-acetic acid from Dr. A. S. C. Lawrence, Cambridge.

The ethyl-dodecyl-acetic acid (Mp. 20-21° C.) and the decyl-dodecyl-acetic acid (Mp. 47° C.) were prepared by Mr. H. K. King, Cambridge.

To all these gentlemen the author wishes to express his thanks.

### Results

#### A. Acids in undissociated form on acid (0.01 N HCl) substrate.

1. Effect of displacing the carboxyl group along a chain of 16 carbon atoms. Isomeric heptadecanoic acids.<sup>2(b)</sup>—Fig. 1 shows that even the introduction of a methyl side chain in the 1:14 acid leads to a considerable expansion of the monolayer. This expansion increases with further increase in the length of the shorter chain to reach its maximum in the 7:8 acid, where the carboxyl group is as near the middle of chain

<sup>6</sup> J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., A*, 1931, 130, 259.

<sup>7</sup> E. Chargaff, *Berichte, B*, 1932, 65, 745.

as possible. The monolayers are liquid and fairly stable, but exhibit in general a slow collapse on standing when the pressure is above 12-15 dynes. As the acids from the 2 : 13 acid on either have their three dimensional melting-points near the temperature of the experiments or are liquids at that temperature, the compression curves show flat collapses due to equilibrium between lenses on the surface and the monolayer. No real equilibrium seems to exist, however, on prolonged standing the pressure usually falls several dynes below the initial collapse pressure. They are thus not very good as piston oils. The initial collapse pressures are fairly

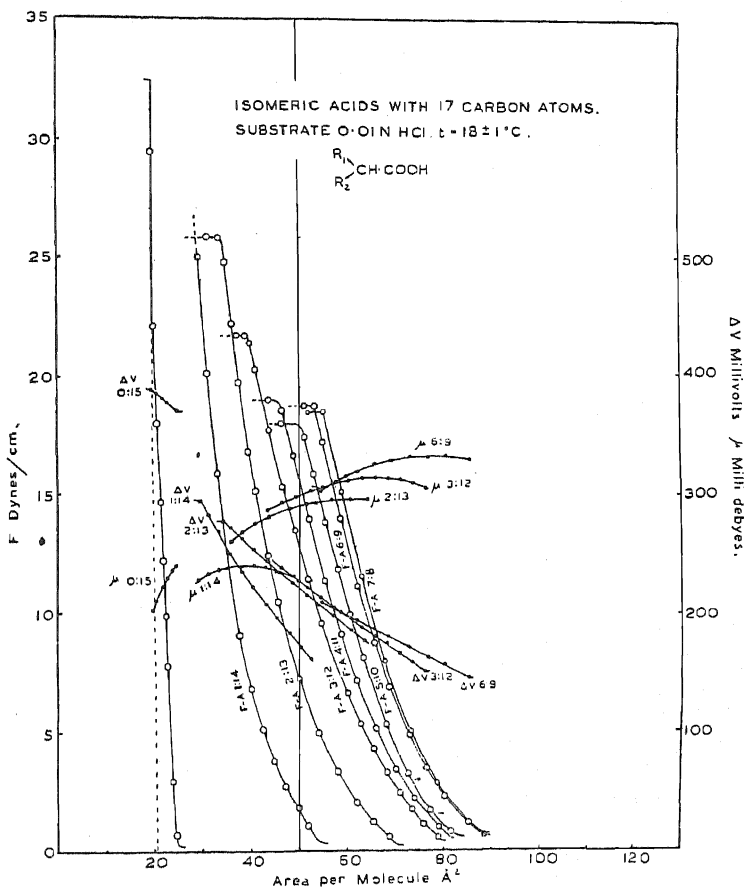


FIG. 1.

reproducible. The limiting area of the 5 : 10 acid, shown in the figure to be at  $83 \text{ Å}^2$ , is uncertain, as this acid expands on standing at low pressures (indicated by small arrows in the figure). The curve in Fig. 1 was obtained on compression immediately after spreading. The same tendency is also found, although less pronounced, in some of the other acids, and has also been found in normal chain acids.<sup>8</sup>

The surface moment  $\mu$  for the 1 : 14 acid is nearly the same as for the straight chain acid, but it increases with increasing expansion and is around 300 millidebyes for the more symmetrical acids. On compression the moment increases first, passes through a maximum and then falls.

<sup>8</sup> G. C. Nutting and W. D. Harkins, *J. Amer. Chem. Soc.*, 1939, **61**, 1180.



This behaviour is characteristic for most di-substituted acetic acids. In order not to overcrowd the figure some of the intermediate  $\Delta V$  and  $\mu$  curves are left out.  $\Delta V$  and  $\mu$  for the 7:8 acid are very similar to those of the 6:9 acid.

2. Effect of increase of the number of carbon atoms in the molecule when the length of the shorter side chain is constant.  $C_{14}$ - $C_{26}$  acids <sup>2(a), (g), (h), 7</sup>.—Figs. 2 and 3 show sets of curves obtained with acids with the shorter chain 1-6 carbons long. The isomeric acids containing 14 carbon atoms (4:8, 5:7, 6:6 of Fig. 3) tend to the vapour expanded state and are unstable at higher pressures. The dotted part of the curves and the flat collapses at about 21 dynes are obtained on rapid compression. The 6:6 acid, although rapidly collapsing above 10 dynes,

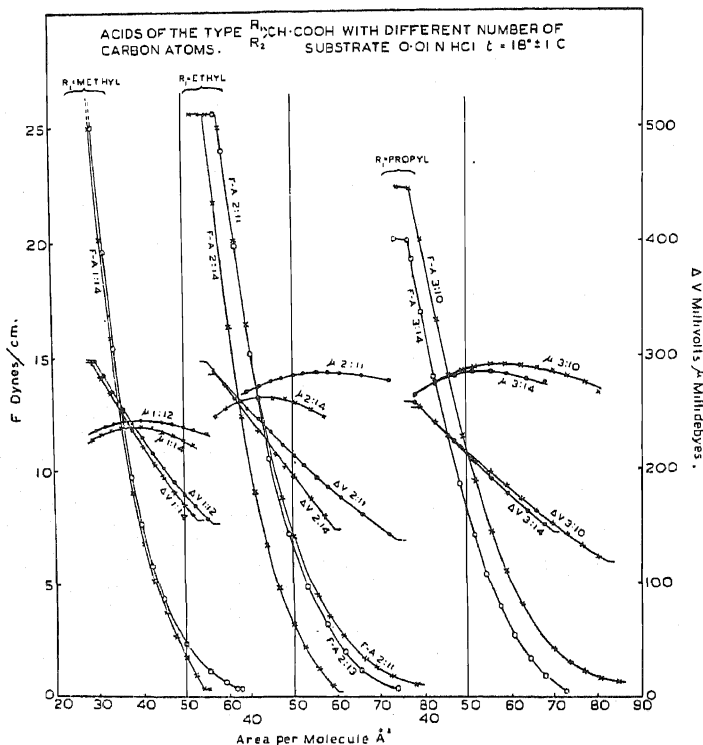


FIG. 2.

also gives a flat collapse at 21 dynes, on very rapid compression. Increase in the total number of carbon atoms has in all cases a condensing effect on the lower part of the curve. At higher pressures there is a condensing effect with 1-3 carbons in the short chain and a tendency to expansion when the side chain is longer. The expansion with increasing length of the short chain is illustrated by the increasing height at which the sets of curves cut the vertical line drawn through the 50  $\text{\AA}^2$  mark on the abscissa. The 4:20 acid, which has a total of 26 carbon atoms, collapses against 0.1 dynes pressure at 18° C. The lateral adhesion between the  $C_{20}$  chains is probably sufficient to remove the polar group from the water when the monolayer is compressed. The adhesion can be reduced by increasing the temperature and at 40° C. to the monolayer withstands 3 dynes pressure (Fig. 3).—The difference in the area occupied by the 2:14 and the 2:13 acids appears a little large for a difference of only one carbon

atom. It has, however, been repeatedly obtained with the specimen available.

The 10 : 12 acid has a limiting area of  $76 \text{ \AA}^2$ , and collapses at an area of  $61 \text{ \AA}^2$  and a pressure of 11 dynes.

The moments increase from methyl to propyl side chains and are then rather constant around 300 millidebyes.

**3. Symmetrical acids with different number of carbon atoms.**—The condensing effect at low pressure and the expansion at higher pressure (*i.e.* the decreasing compressibility) with increasing number of carbon atoms are well illustrated by the curves in Fig. 4. The compressibility per  $\text{CH}_2$  group appears to be roughly constant. The stability of the 12 : 12

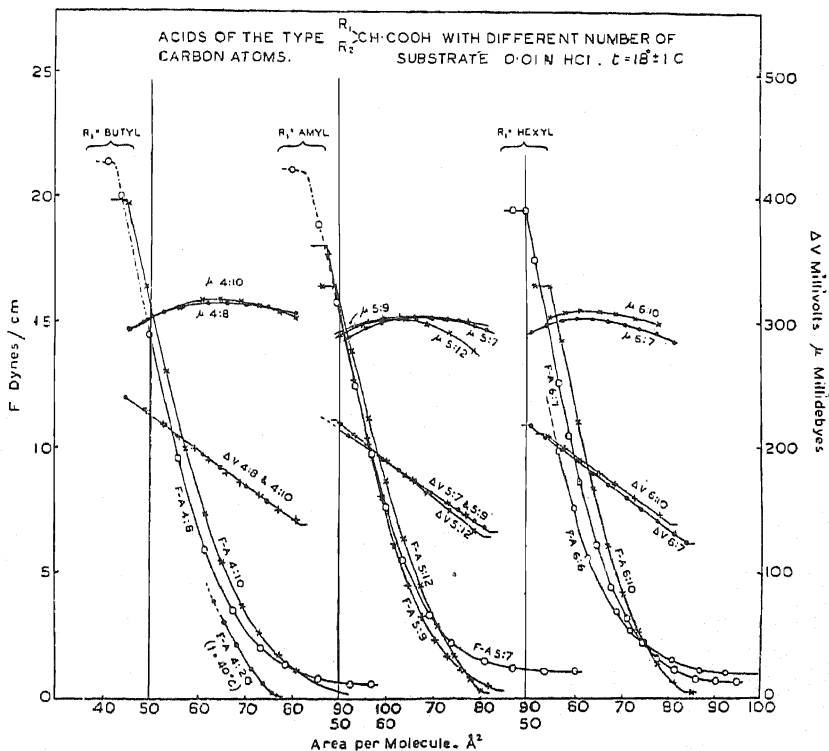


FIG. 3.

acid with 26 carbon atoms is rather poor, its surface potential and moment are similar to those of the 10 : 14 acid. The 18 : 18 acid with 38 carbon atoms was found to give no stable monolayer.

**4. Isomeric acids with 26 carbon atoms.**<sup>7</sup>—With 26 carbon atoms (Fig. 5) the hydrophobic part of the molecule outweighs the hydrophilic group and the monolayers are rather unstable. The stability in this case seems to be greatest when the number of carbon atoms in the longer chain is twice that of the shorter chain. Even in this case the most symmetrical acid is the most expanded.

**5. Acids with saturated hydrocarbon rings in  $\alpha$ -position** <sup>2(a), (b), (c), (f).</sup> Cyclopropylmethyl-tetra-decanoic and cyclopentyl-tridecanoic acids ( $\text{C}_{18}$ ) and cyclobutylmethyl-tetradecanoic and cyclohexyl-tridecanoic acids ( $\text{C}_{19}$ ).—Fig. 6 shows that cyclopentyl and cyclobutylmethyl in  $\alpha$ -position give almost identical curves, which is to be expected. Cyclopropylmethyl decreases and cyclohexyl increases the expansion

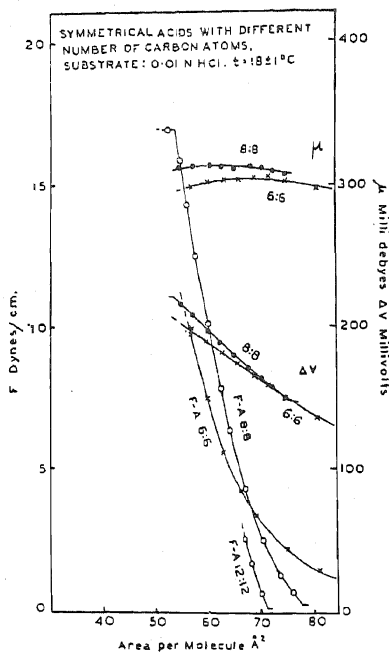


FIG. 4.

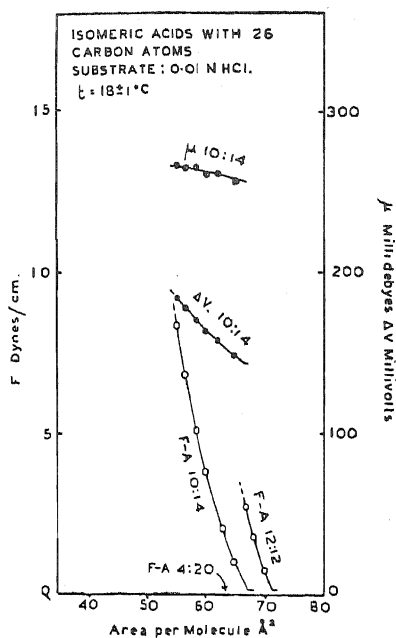


FIG. 5

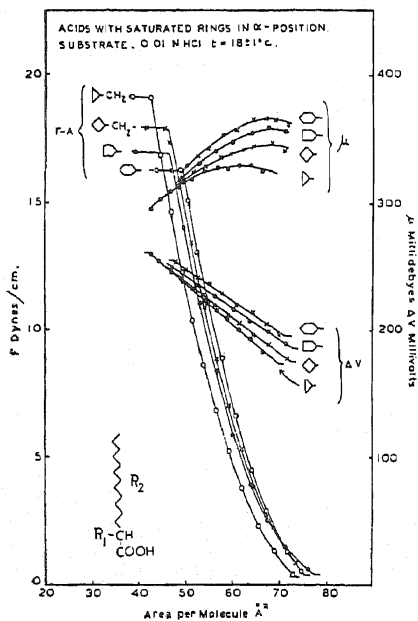


FIG. 6

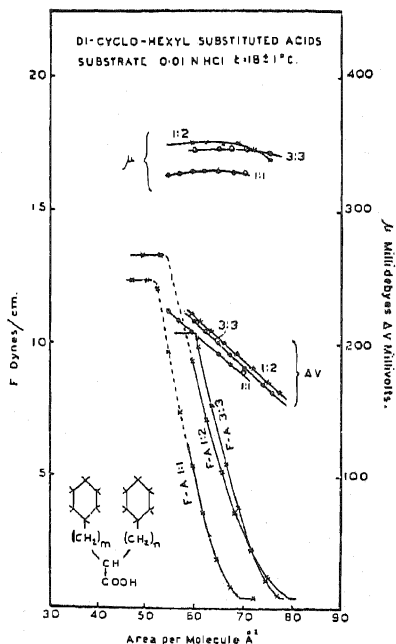


FIG. 7.

slightly. The area of the cyclohexyl ring is  $30 \text{ \AA}^2$  according to measurements by Danielli<sup>9</sup> on long chain cyclohexanols. The  $\alpha$ -cyclohexyl-tridecanoic acid collapses at just below  $50 \text{ \AA}^2$ , which corresponds roughly to the area of a cyclohexyl group + a hydrocarbon chain. The  $F$ - $A$  curve of this acid is completely reversible; even if the acid has been compressed beyond the collapsing point, the pressure on expansion falls along the original compression curve. In general, the acids studied on expansion after collapse give slightly smaller areas than on the initial compression. The area so obtained also depends on the rate of expansion.

**6. Di-cyclohexyl substituted acids.**<sup>2(d)</sup>—(The numbers in Fig. 7 refer to the number of  $-\text{CH}_2-$  groups in the two branches respectively.) The acids occupy somewhat larger areas than those of the preceding group, and are not stable below  $60 \text{ \AA}^2$  per molecule, when the two cyclohexyl rings are squeezed up against each other. The monolayers stand only comparatively low pressures. The surface moments  $\mu$  for acids containing saturated rings is 300–350 millidebyes and are slightly higher than those generally obtained for acids with straight branches.

## B. Acids on neutral substrates.

**Effect of hydrogen ion concentration and of divalent ions.**—Fig. 8 shows the  $F$ - $A$  curves for two acids on different substrates. On M./25 phosphate buffer, pH 7.2, the acids tend to the vapour expanded state. The stability of the branched chain acids monolayers on neutral substrates is rather poor, although some higher acids ( $\text{C}_{24}$  and  $\text{C}_{28}$ ) are slightly more stable than on acid solution. Introduction of Ca ions in the form of tap water (Cambridge tap water, pH 8, Ca as bicarbonate about  $2 \times 10^{-3} \text{ M.}$ ) has a slight condensing effect on the whole  $F$ - $A$  curve. As is to be expected, the surface potential decreases with increasing ionisation of the carboxyl group. The monolayers studied in this investigation are nearly all of the liquid expanded type. Fig. 8 shows the thermal expansion of a typical acid. The curves are obtained without use of enclosed constant temperature apparatus, and show only the general type of expansion obtained.

The 6:6, 7:8 and 1:14 acids have also been examined using the automatic registrating Wilhelmy surface balance described by Dervichian.<sup>10</sup> The results confirmed those obtained in the ordinary way.

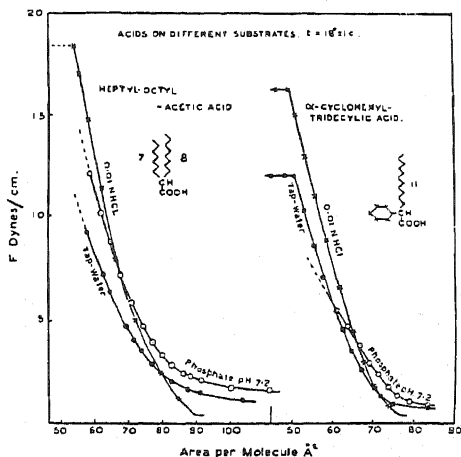


FIG. 8.

## Discussion.

The fact that the monolayers tend to expand with increasing number of carbon atoms, when the shorter chain contains more than 3 or 4 carbons, shows that two long hydrocarbon chains attached to a common (tertiary) carbon atom do not arrange themselves side by side easily.

<sup>9</sup> N. K. Adam, J. F. Danielli, et al., *Biochem. J.*, 1932, **26**, 1233.

<sup>10</sup> (a) D. G. Dervichian, Thésés, Paris, 1936, Masson et C<sup>ie</sup>; (b) *idem. J. Physique*, 1935, **6**, 221.

This is particularly marked in the symmetrical acids shown in Fig. 4. One would expect the 12:12 acid to be more condensed than the 8:8 acid due to increased adhesion between the two longer chains, but on the contrary it is rather more expanded. The areas are very much larger than that occupied by two closely packed chains, 40 Å<sup>2</sup>. This behaviour will be further discussed in Part II.

The apparent surface dipole moment  $\mu$  increases with increasing expansion. This has also been found in other cases, for instance for

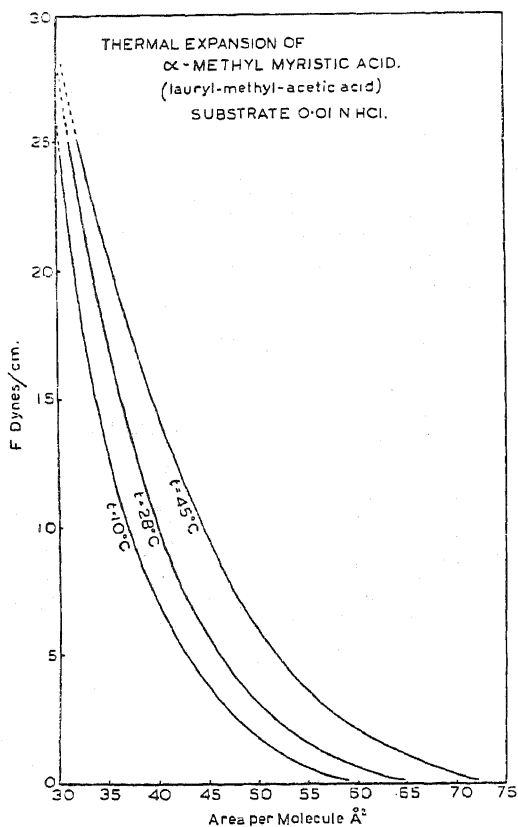


FIG. 9.

esters and methyl ketones,<sup>11</sup> and can be attributed to reorientation of the dipole axis with increased expansion and possibly also a change in the dielectric constant at the interphase. The moment of a normal chain acid as the myristic acid in the expanded state is around 200 millidebyes,<sup>12</sup> and does not differ appreciably from that of normal chain acids in the condensed state.

The considerable increase of the moment in branched acids at corresponding areas is therefore probably due to a change in orientation of the polar group caused by the  $\alpha$ -substitution, when the substituent is larger than a methyl group. For the same degree of expansion the C<sub>24</sub> and C<sub>28</sub> acids show slightly smaller moments than their lower homologues.

The relative expansion at low surface pressures and contraction at higher pressures on a neutral substrate seems to be a general phenomenon for expanded fatty acids; it occurs both in cases of thermal expansion as in the myristic acid<sup>13</sup> and of expansion due to steric reasons as in unsaturated acids,<sup>14</sup> and in the branched chain acids under discussion.

<sup>11</sup> (a) J. H. Schulman and A. H. Hughes, *Proc. Roy. Soc., A*, 1932, 138, 430. (b) A. E. Alexander and J. H. Schulman, *ibid.*, A, 1937, 161, 115. (c) N. K. Adam, J. F. Danielli and J. B. Harding, *ibid.*, 1934, 147, 491.

<sup>12</sup> *Loc. cit.* <sup>11a</sup> and *loc. cit.* <sup>10a</sup>.

<sup>13</sup> W. D. Harkins and R. J. Myers, *J. Chemical Physics*, 1936, 4, 716.

<sup>14</sup> J. Marsden and E. K. Rideal, *J. Chem. Soc.*, 1939, 1163.

The expansion at low pressure was attributed by Harkins and Myers<sup>13</sup> to repulsion of ionised head groups but the reason for the contraction is more obscure. Marsden and Rideal<sup>14</sup> attribute it to accumulation of bound ions on compression of the monolayer and to association as found in acid soaps. It is doubtful if this can be the cause in branched acids where the area of the monolayer at collapse is more than  $50 \text{ \AA}^2$  per molecule, *i.e.* the distance between the polar groups is large, but the slight general contraction when calcium ions are present in the substrate indicates effects of ions even when the distance between the heads is large. Calcium ions are not, however, sufficient to condense the acids at low pressures, the strong condensing effect found for straight chain acids being entirely absent.

In the fully ionised state, *pH* 11 or higher, branched chain acids give vapour films due to the strong repulsion between the head groups, while straight chain acids, probably due to salt effects,<sup>15</sup> give vapour films only on extremely alkaline solutions.

Adams and collaborators found that a number of their synthetic acids had the same action as chaulmugric acid on the leprosy bacillus.<sup>16</sup> Very dilute soap solutions of the acids killed the bacillus *in vitro*. It was found that acids with 16 carbon atoms were the most effective. The hydrocarbon part of the molecule must be branched but the special configuration does not seem important. Neither this investigation nor the surface tension measurements of Stanley and Adams<sup>17</sup> on soap solutions give any direct clue to this behaviour. Two facts may be important in this connection, however: (1) 16 carbon atoms probably give an optimal balance between hydrophilic and hydrophobic properties of a carboxylic acid; and (2) the branched chain prevents close packing and formation of strong complexes with compounds having normal chains, due to weakening of the van der Waals' and polar forces between the molecules. The latter point is also important for the micelle formation in the soap solutions. The tendency to form micelles is far less and the water solubility far higher for branched than for normal acids.<sup>17</sup>

The author is indebted to Professor E. K. Rideal and Dr. J. H. Schulman for their interest in the work, and to Dr. D. G. Dervichian, Paris, for carrying out the experiments using the Wilhelmy balance.

### Summary.

Force-area and surface potential—area relations are given for a number of branched chain carboxylic acids of the di-substituted acetic acid type, with a total number of carbon atoms from 14 to 38. For unionised aliphatic acids the following applies:

- (a) The monolayers are of the liquid expanded type, with the exception of the  $C_{14}$  acids, which are vapour expanded.
- (b) For a given number of carbon atoms the monolayers become more expanded with the displacement of the carboxyl group from the end to the middle of the chain, *i.e.* with increasing symmetry of the di-substituted acetic acid.

<sup>13</sup> (a) N. K. Adam and J. Miller, *Proc. Roy. Soc., A*, 1933, 142, 401. (b) J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, 1938, 34, 748.

<sup>14</sup> *Loc. cit.* <sup>2</sup> and W. M. Stanley, G. H. Coleman, C. M. Greer, J. Sacks and R. Adams, *J. Pharmacol.*, June, 1932.

<sup>17</sup> W. M. Stanley and R. Adams, *J. Amer. Chem. Soc.*, 1932, 54, 1548.

- (c) Increase in the total number of carbon atoms has a condensing effect at low surface pressures, and also at higher pressures if the short chain contains less than 4 carbon atoms; if longer, expansion occurs at higher pressures.
- (d) The apparent surface moment  $\mu$  tends to increase with increasing expansion.

Acids containing alicyclic rings are, due to the size of the rings, very expanded, and show comparatively high surface moments.

On neutral substrates the monolayers undergo a relative expansion at low pressures, and a contraction at higher pressures. Ions of divalent metals have a slight condensing effect on the whole force-area curve.

In the fully ionised state, on substrates having a  $pH$  of 11 or higher, the acids give vapour films.

*The Colloid-Science Department,  
The University,  
Cambridge.*

## NOTE ON HEATS OF FORMATION OF ETHYL AND PROPYL PEROXIDES.

BY E. C. STATHIS and A. C. EGERTON.

*Received 28th February, 1940.*

Although the measurements given in this note are only of a preliminary kind, it seems worth while to record them, as it may not be possible for some time to complete the investigation of the thermal properties of these peroxides as was intended.

The peroxides were made by methods described elsewhere, A. C. Egerton, F. L. Smith, A. R. Ubbelohde, *Phil. Trans.*, 1934, 234, p. 433; E. J. Harris and A. C. Egerton, *Proc. Roy. Soc. A*, 1938, 168, p. 1; E. J. Harris, *Proc. Roy. Soc. A*, 1939, 173, p. 126.

The heats of combustion were determined in a bomb calorimeter. About 0.5 gram of the peroxide was weighed into very thin glass bulbs with ground-in stoppers, which it filled completely. The bulb was placed in a small porcelain crucible; a cover glass perforated with a central hole held it in position. Ignition was started by an iron wire touching 0.1 gram sugar spread on the tray formed by the cover glass. A number of experiments led to the following results for the heats of combustion at 298° K. and 1 atmos. :—

$(C_2H_5)_2O_2$	.	.	.	.	.	7155 $\pm$ 200 cal. per gram.
$C_2H_5O_2H$	.	.	.	.	.	5400 $\pm$ 200    "    "
$C_3H_7O_2H$	.	.	.	.	.	6300 $\pm$ 200    "    "

These results provide values for the heat of formation of the vapours, which are only little different from the values for the corresponding ether and alcohols :—

$(C_2H_5)_2O_2$	.	68 Kg. cal. per mol.	$(C_2H_5)_2O$	.	65 Kg. cal. per mol.
$C_2H_5O_2H$	.	50   "   "   "	$C_2H_5OH$	.	57   "   "   "
$C_3H_7O_2H$	.	60   "   "   "	$C_3H_7OH$	.	63.5   "   "   "

It was hoped to check and obtain more reliable figures by hydrogenation and other methods, so that the energy associated with the peroxide bond could be assessed.

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South Kensington, S.W. 7.*

## REVIEWS OF BOOKS.

**Ephraim's Inorganic Chemistry.** 3rd English Edition. By P. C. L. THORNE and A. M. WARD. (London: Gurney and Jackson, 1939. Pp. xii + 911. Price 28s. net.)

This edition of Ephraim is some forty pages longer than the previous one. It has been well brought up to date and, in addition to numerous references to recent papers on the various aspects of the subject treated, there are several entirely new sub-chapters.

Ephraim is now so well established as an advanced text-book and book of reference that extensive review is not called for. Suffice it to say that the standard of the previous edition is fully maintained.

The volume is excellently documented so that the reader can readily refer to the source of any particular piece of information. Well printed and soundly bound, this book is splendid value.

**Statistical Thermodynamics.** By R. H. FOWLER and E. A. GUGGENHEIM. (Cambridge: at the University Press, 1939. 26 × 17 cm.; pp. x + 693. Price, 40s.)

Fowler's *Statistical Mechanics*, the second edition of which was published towards the end of 1936, is remarkable not only for the rigour of the mathematical technique by which the statistical formulæ are developed from the basic quantum mechanical postulates, but also for the vast range of applications which are considered in detail. For most physicists and chemists, however, the book is somewhat formidable, a contributory factor to this being the avoidance of relatively familiar thermodynamic methods. Many will welcome a modified version in which, as the authors state in their preface, the theory is developed so as to be complementary to a presentation of thermodynamics, mathematical details of proofs are taken for granted, and the applications are confined to terrestrial physics and chemistry. Guggenheim's profound grasp of thermodynamical methods, as shown in his *Modern Thermodynamics* (1933), and his wide interests in the general field, shown by his papers, make him eminently fitted for collaboration in the task of providing this modified version of statistical mechanics.

The general approach and character of the treatment follow closely the lines of Fowler's earlier book, many sections of which are taken over with little change. Even in these, however, the changes that have been made suggest that the whole of the material has been subjected to extremely careful revision. Except for the omission of the previous discussions on problems of stellar atmospheres and interiors, and on fluctuations, the field of applications covered is much the same. There has, however, been a tightening up in the general arrangement, the more recent work is fully discussed, and a considerable amount of previously unpublished material is included. A chapter which has no counterpart in the earlier book is



that on generalised partition functions and the related thermodynamic functions and their applications.

The first two of the fourteen chapters discuss the basic assumptions of statistical mechanics, enunciate the general theorems required, and develop the connections between the statistical and thermodynamic formulæ. The statistical procedure used is that of determining average, rather than most probable, values for an assembly, using the elegant contour integration method. Although details of proofs are omitted, the method is fully explained. The statistical problem, in connection with a particular assembly, is reduced to that of constructing and evaluating a partition function; from this the various thermodynamic functions can be derived, and the theoretical molar characteristics of the assembly determined, to be compared with observed molar properties. The second law of thermodynamics is formulated by reference to the (Helmholtz) free energy function (rather than the entropy function), and by a process of identification of the terms in a statistical function which is shown to have the same properties, the thermodynamic significance of the parameters occurring in the statistical treatment is obtained.

Applications are first made to permanent perfect gases. There is a clear discussion of nuclear symmetry effects, and detailed treatments are given of the rotational and vibrational heat capacities for a large number of molecules. Crystals are then considered, primarily on the lines of the Debye treatment, with discussions on the character and effect of the approximations made. A long chapter on chemical equilibria and evaporation concludes with a clear and detailed discussion of the status of Nernst's heat theorem. The account of grand partition functions which follows should be of value in clarifying the physical meaning of various generalised partition functions and the associated thermodynamic functions, and in showing the circumstances in which alternatives to the usual partition functions may advantageously be employed. The discussion of imperfect gases includes an analysis of interaction energies, and accounts of very recent work on condensation. Liquids are treated in two chapters, dealing with non-electrolytes and electrolytes. The more recent work in which a liquid is regarded as quasi-crystalline rather than as quasi-gaseous is fully described, and an account is given of the application of grand partition functions to liquid mixtures. There is an excellent presentation and critical discussion of the Debye-Hückel treatment of electrolytes, and of later theoretical developments. In the chapter on surface layers, mobile and localised monolayers are discussed.

The basic principles of the modern electron theory of metals are considered, the fundamental formulæ are derived, and applications are made to electronic heat capacities, thermionic emission and the photo-electric effect. Here and in the last chapter use is made of the formulæ essentially characteristic of Fermi-Dirac statistics; in all the applications in other chapters the quasi-classical approximations are adequate.

Very properly, a chapter on chemical kinetics has been included. This is not only of interest in itself, but is almost indispensable for providing a quantitative guide as to the conditions for applicability of the results of equilibrium theory with which the book is primarily concerned.

The range and power of statistical methods is shown clearly in the last two long chapters. The first of these deals with lattice imperfections, and

order-disorder phenomena in alloys. The chapter is notable for the very detailed account of the relation between the treatments of order-disorder effects due to Bragg and Williams, Kirkwood, and Bethe, and the development of a new "quasi-chemical" treatment which enables a good approximation to be obtained without undue complexity of mathematical method. The final chapter deals with electric and magnetic properties. The treatment of electric and magnetic susceptibility includes a review of crystalline field effects in paramagnetic salts, a discussion of the magnetic cooling method, and some account of the interpretation of phenomena in the very low temperature region. An account is also given of the collective electron treatment of ferromagnetism.

The above indication of the topics treated can give but an inadequate impression of the character and content of this book. Each chapter may be said to constitute a monograph on the subject with which it is concerned, giving a detailed presentation of theoretical investigations, and an adequate summary of relevant experimental data. Although the book has, in one sense, the character of an extended series of reports, in another it is original throughout, for all the work discussed is presented from the unifying standpoint provided by the general statistical treatment.

Attention should perhaps be directed to the point that, when the book is described in a sub-title as "a version of Statistical Mechanics for Students of Physics and Chemistry", the wider meaning of "students" must be understood. In no sense is this an introductory treatise. It could hardly serve as a guide to students making a first approach to the subject, and it is not concerned, save incidentally, with the historical development. It is an exposition of a technique for the application of statistical mechanics to physico-chemical problems, and of a large number of the applications which have been made, the character of the treatment implying the assumption of much more than elementary knowledge of the field on the part of readers. The general methods used, moreover, though they are, from the standpoint of mathematical rigour, perhaps the most satisfactory available, will undoubtedly make severe demands on many physicists and chemists. Readers will, however, be amply repaid for such efforts as are required of them. A growing appreciation of this book for the magnificent achievement which it is will go hand in hand with a clearer and more profound understanding of the wide range of physico-chemical phenomena with which it deals.

E. C. S.

**Molecular Spectra and Molecular Structure. I. Diatomic Molecules.**

By G. HERZBERG. Translated by J. W. T. SPINKS. (New York: Prentice-Hall, Inc., 1939. Pp. xxvi + 592, with numerous illustrations and tables. Price \$6.50.)

This comprehensive work has already received attention in these *Transactions*, at the time of its issue in the original German edition. It is therefore unnecessary to enlarge upon its merits, which are there for all to see. The translation which has now appeared has been undertaken with the author's co-operation, an advantage which is manifested by the way in which the sense of continuity of style has been happily preserved. A book of this calibre should be a stimulus to refined experiment, because what is most urgent in molecular spectroscopy to-day is the provision of

data of the greatest possible degree of precision, combined with the highest resolving power. This is what the theorist needs, and this volume illustrates what he can do with it as soon as it is forthcoming.

F. I. G. R.

**Kinetik der Phasenbildung.** By M. VOLMER. (Pp. xii and 220. Verlags. Theodor Steinkopff, Dresden, 1939. Price R.M. 14.25 : bound 15.0.)

This book forms the fourth volume of a series with the general title *Die Chemische Reaktion*, issued under the editorship of Professor Bonhoeffer.

It deals in as systematic a way as possible with the phenomena which accompany the passage of matter from one to another of its states of aggregation. The treatment is clear and balanced. Mathematical calculations are given throughout, but they do not outweigh the qualitative and descriptive part of the book.

After a historical introduction the transitions gas-liquid, gas-solid, crystal I-crystal II, and so on, are discussed in order : then delayed transitions and nucleus formation are dealt with and drop and bubble formation treated at length. Finally, there are short chapters on the rule of "steps" and on the structure of new phases (crystallite size and so on).

The book is a very useful contribution to the literature of molecular processes ; numerous topics of importance are discussed in a logical and judicial manner. The difficult task of a really synthetic treatment of the whole is not attempted ; the author would probably not regard this as possible or desirable at the present time.

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#### ERRATA.

P. 329. Formula 1. The methyl radical of the acetyl group has been omitted.

P. 506. Line 7 from bottom. For "specification" read "specific action".

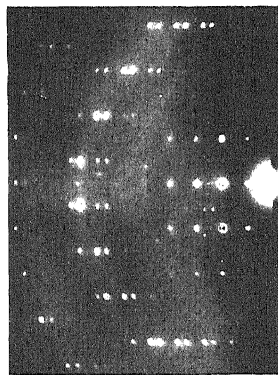


FIG. 1.—Nickel oxide condensed on to heated corundum;  $\{112,0\}$  face  $[001]$  azimuth of the corundum;  $\{111\}$  face  $\langle 112 \rangle$  azimuth of the nickel oxide.

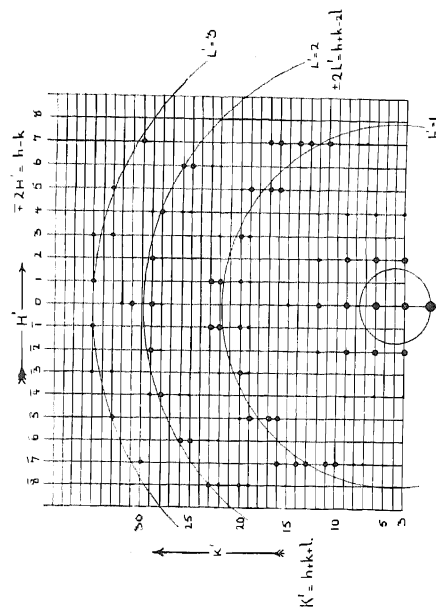


FIG. 2.—Index diagram to Fig. 1.

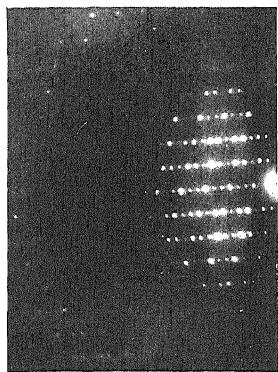


FIG. 3.—Surface as for Fig. 1. Azimuth  $30^\circ$  from Fig. 1.

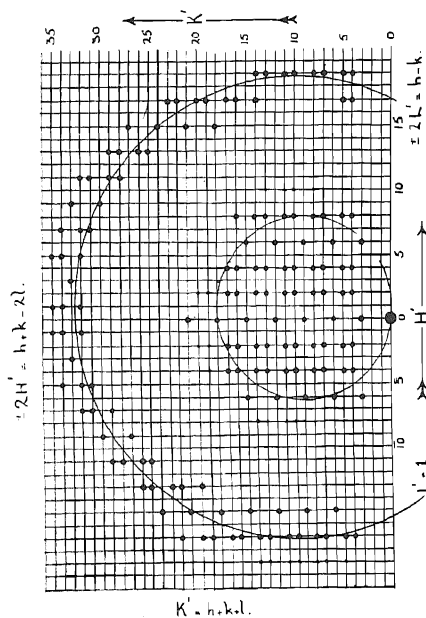


FIG. 4.—Index diagram to Fig. 3.

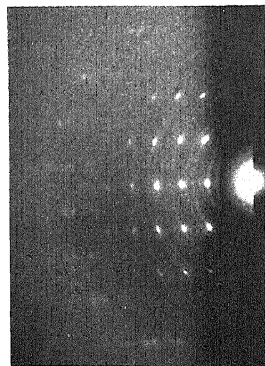


FIG. 7.—Nickel oxide condensed on to corundum;  $(000.1)$  face  $[1\bar{c}0]$  azimuth of corundum;  $\{111\}$  plane  $\langle 112 \rangle$  azimuth of nickel oxide.

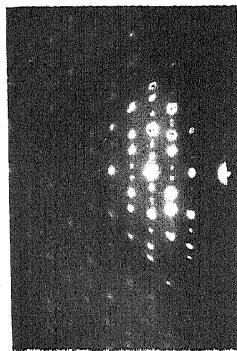


FIG. 10.—Nickel oxide condensed on to corundum  $(10\bar{1}.1)$  face and azimuth  $90^\circ$  from the rhombohedral edge  $[12\bar{1}]$  of the corundum;  $\{110\}$  plane  $\langle 001 \rangle$  and  $\langle 111 \rangle$  azimuths of nickel oxide.

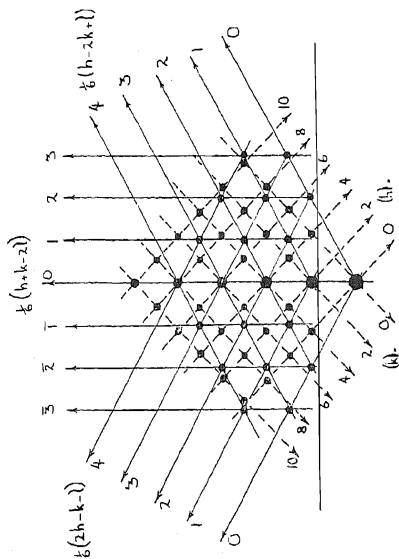


FIG. 11.—Index diagram to Fig. 10.

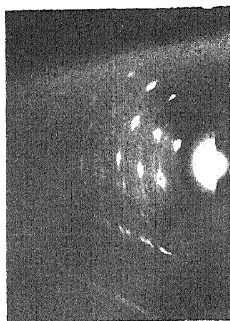


FIG. 12.—Nickel oxide on a plane of corundum inclined by  $30^\circ$  to the basal plane,  $[100]$  azimuth of corundum,  $[112]$  of nickel oxide. Cf. Fig. 7.

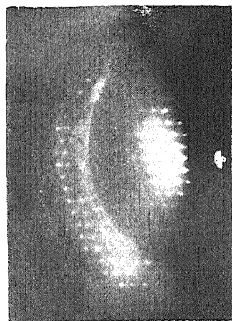


FIG. 15.—Pattern from specimen of Fig. 3 after heating,  $[110]$  azimuth of nickel aluminate, only one orientation present.

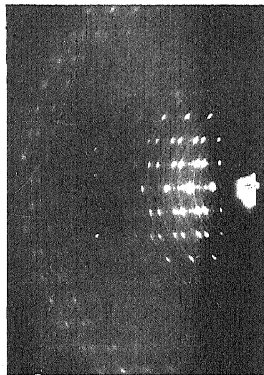


FIG. 8.—Azimuth  $30^\circ$  from Fig. 7.

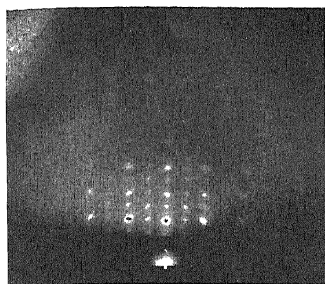


FIG. 16.—Pattern from specimen of Figs. 7 and 8 after heating,  $\langle 112 \rangle$  azimuths of nickel oxide and aluminate.

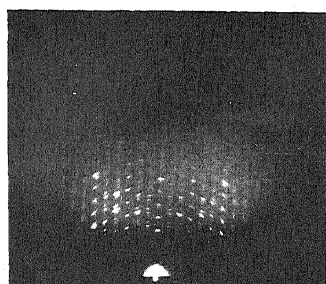


FIG. 17.—Pattern from specimen of Fig. 16 after further heating,  $\langle 110 \rangle$  azimuth of nickel aluminate; nickel oxide pattern faintly visible.

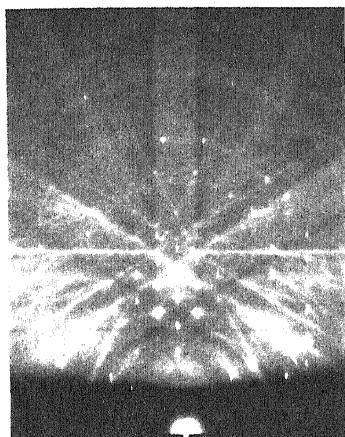


FIG. 18.—Kikuchi-line pattern from corundum surface about  $6^\circ$  from  $\{112,0\}$ , after polishing, "annealing," and lightly etching. Prominent zone axis is  $[001]$ . Bands at  $0^\circ$   $60^\circ$  and  $120^\circ$  from horizontal are  $112,0$  type, and those at  $30^\circ$ ,  $90^\circ$ , and  $150^\circ$  are  $101,0$  type.

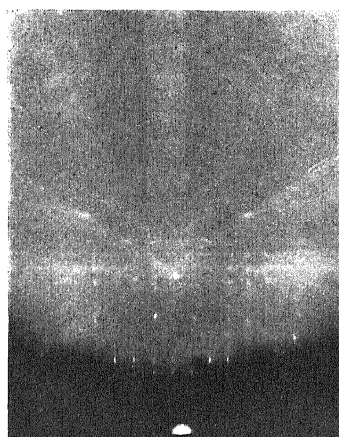
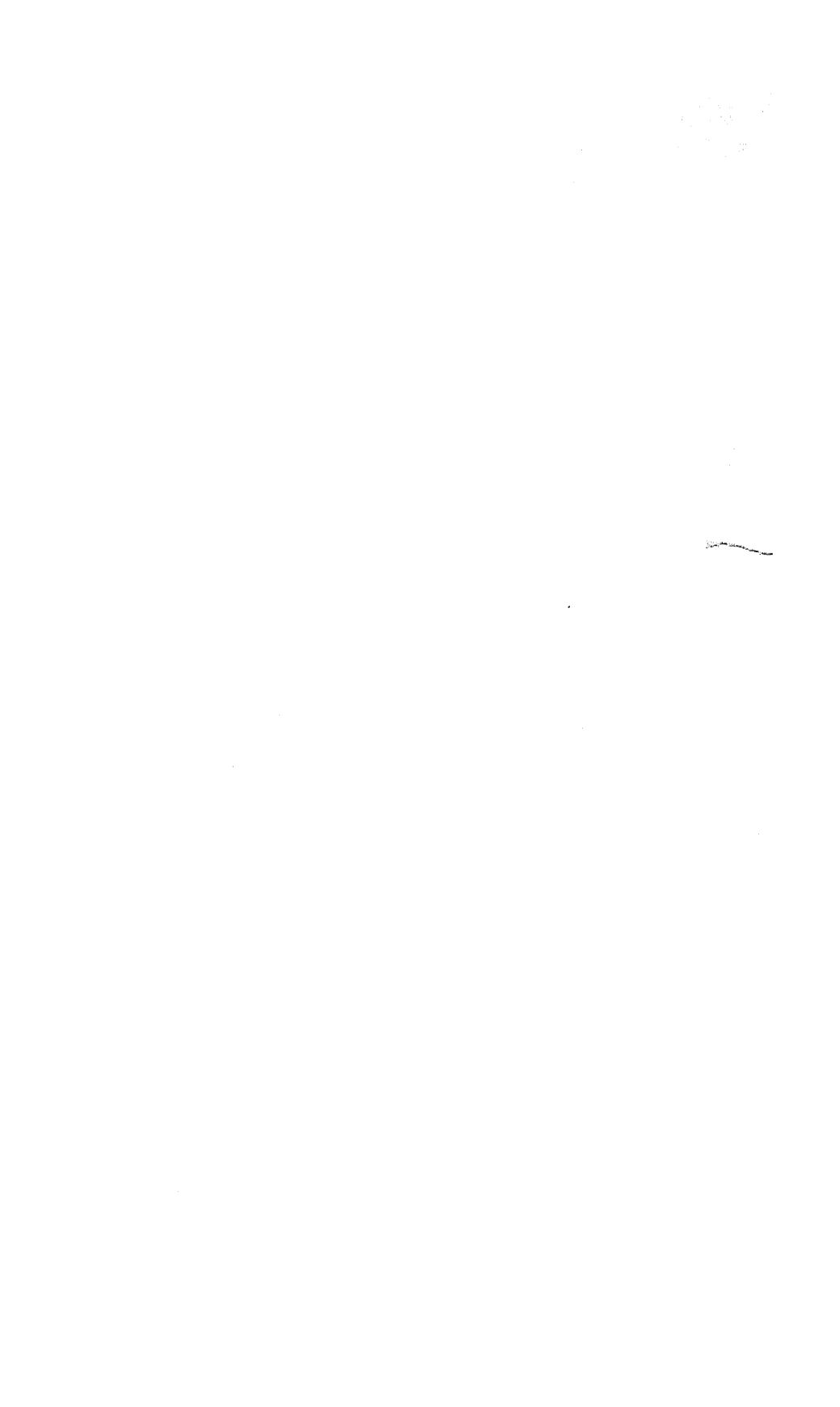


FIG. 19.—Pattern from specimen of Fig. 18 with a thin film of nickel aluminate on the surface.





## DEGRADATION OF LONG CHAIN MOLECULES.

BY H. MARK AND R. SIMHA.

*Received 18th December, 1939.*

The chemical decomposition of large molecules has raised considerable interest during the last few years. It has been possible in a considerable number of cases to work out a complete reaction scheme for the chemical or thermal decomposition of organic molecules which include quite a number of steps, each of which was characterised by an activation energy and a frequency constant or collision number.<sup>1</sup> In particular, the degradation of chain molecules has been considered and the break of certain linkages in them has been followed by quantum mechanical observations.<sup>2</sup>

If one passes to very large particles, especially to long chain molecules, a dynamical treatment seems to be far too complicated and difficult to have any chance of success. On the other hand, a statistical method may be successful in such cases if certain conditions prevail.

Several years ago H. Hopff, K. H. Meyer, and H. Mark<sup>3</sup> found indications that the hydrolytic degradation of starch can be followed with a fair degree of accuracy by assuming that all hydrolysable bonds in the large molecules are broken during the decomposition reaction at approximately the same rate and, hence, that the total process can be calculated by a comparatively simple equation. A more complete treatment of this problem was given by K. Freudenberg and W. Kuhn,<sup>4</sup> who studied under various conditions the degradation of cellulose and compared their results very carefully with a number of relations which Kuhn had derived from statistical considerations. They found that best agreement with the experiment was reached on the assumption that all the links of a long chain are opened according to the same reaction constant except the few links at the end of the chain.

Later, Flory<sup>5</sup> took up again the problem of the statistical treatment of degradation reactions practically under identical conditions and compared his formulæ with the results of experimental polycondensation processes.

An outstanding feature of this calculation is the fact that, if one starts degradation with an entirely homogeneous material, for instance with  $N$  chains each having  $n$  links, one initially has an entirely sharp distribution curve of the starting material. One has an equally sharp distribution curve at the end of the process if all the initial substance is

<sup>1</sup> Cf. e.g. F. O. Rice and K. F. Herzfeld, *J. Chem. Physics*, 1939, **7**, 671; F. O. Rice and W. D. Walters, *ibid.*, 1015.

<sup>2</sup> M. Polanyi and E. Wigner, *Z. physik. Chem. A*, 1928, **139**, 439; H. Pelzer, *El. Chem.*, 1933, **39**, 608.

<sup>3</sup> K. H. Meyer, H. Hopff and H. Mark, *Ber.*, 1929, **62**, 1103; cf. also R. O. Herzog and O. Kratky, *Naturw.*, 1930, **18**, 732.

<sup>4</sup> K. Freudenberg and co-workers, *Ann.*, 1928, **460**, 288; *Ber.*, 1930, **63**, 1510; W. Kuhn, *ibid.*, 1503; *Z. physik. Chem., A*, 1932, **159**, 368; K. Freudenberg and W. Kuhn, *B.*, 1932, **65**, 454.

<sup>5</sup> J. P. Flory, *J. Am. Chem. Soc.*, 1936, **58**, 1877; cf. also W. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 39.



degraded down to a monomeric material. In this case one has  $N \cdot n$  molecules of the monomeric substance which are strictly identical with each other. However, intermediately one has mixtures of chains with quite different lengths; in this way one passes from a homogeneous starting material over a wide range of mixtures again to a homogeneous end product. This is in accordance with the fact that also during a multi-stage decomposition reaction of a low molecular substance a great number of intermediate compounds—molecules, radicals, atoms, etc.—are formed which we would find if we could analyse the reaction mixture at any time wanted.

In order to get some experience on the behaviour of long molecular compounds during their degradation a series of experiments was started in 1935 at the 1st Chemical University Laboratory in Vienna. The aim was first to prepare homogeneous starting materials for degradation processes, which was partially done by polymerising styrene, vinyl acetate, and acrylic ester under conditions which were favourable for homogeneous end products. These substances were then depolymerised thermally and the decomposition followed quantitatively. Secondly, technical cellulose acetate, cellulose nitrate, and ethyl cellulose were fractionated in comparatively large quantities, and fairly homogeneous starting materials for hydrolytical degradation experiments obtained. These samples were then degraded and distribution curve was followed quantitatively.\*

To compare with theoretical expressions the results obtained one has to rely upon the equation of Kuhn and Flory. This relation, however, is derived on the assumption that the original chain length was infinite, which certainly does not hold in the above-mentioned experiments. Of course, if interest is concentrated upon the end of the degradation process and upon the distribution of very low members of the polymer homologous series which is produced during the reaction, one may neglect the influence of the original chain length. To get quantitative information regarding the relative amount of longer chains during the initial stages of the degradation process, however, one has to take into account the length of the original chains.

This improvement of the theoretical treatment of the polymeric degradation reaction was introduced by R. Simha,<sup>6</sup> who derived a formula which seems to be competent for the quantitative features of a decomposition reaction throughout the whole process.

In the following, first a short derivation of this formula will be given and then the above-mentioned experiments will be illustrated more extensively and compared with the results of the theoretical considerations.

### 1. A Statistical Formula for the Degradation of Long Chains.

Kuhn and later Flory have developed very clearly an expression which describes the degradation of long chains under the assumption that the length of the original chain is infinite and that all links are split with the same probability.

\* The writers desire to express their gratitude to Dr. J. W. Breitenbach, Dr. F. Breuer, and Dr. E. Marecek who carried out the degradation and fractionating experiments.

<sup>6</sup> R. Simha, Abstract of papers, 98th Meeting of the Am. Chem. Soc., Boston, Mass., 1939; cf. also K. H. Meyer and H. Mark, *Highpolymeric Chemistry*, second edition, 1st volume, p. 318, Elsevier Publishing Co., 1940.

If  $n$  be the number of bonds which are originally present,  $n$  being a very large number, then we have a chain of  $(n + 1)$  members. We now assume that by an entirely random process  $r$  of these links are opened and hence  $(n - r)$  remain closed. Under such conditions one can define a degree of degradation  $\alpha$  by

$$\alpha = \frac{r}{n}. \quad (1)$$

The probability that a single individual link is opened during the whole process is apparently equal to  $\alpha$ , the probability that it is left untouched consequently is equal to  $(1 - \alpha)$ .

If we want to cut out a chain of  $s$  links from the original chain of infinite length we have first to break one link, then to leave  $s$  links unbroken, and finally open one link again. According to Kuhn's consideration the probability for this composed process is given by the product of the probability for each elementary step of it.

If the original chain is very long compared with the one which is broken out of it, the result is given by the following equation

$$w_s = \alpha \cdot (1 - \alpha)^s \cdot \alpha. \quad (2)$$

Each factor  $\alpha$  stands for the probability of cutting the two ends of the new chain out of the original one and each factor  $(1 - \alpha)$  stands for the fact that the new chain should have  $s$  links in continuo.

It is easy to see how this consideration has to be changed if the length of the initial chain and the length of the one which has to be cut out are of the same order of magnitude, which means that  $n$  and  $s$  are of similar value.

In this case the probability for the first step, namely to cut the initial chain at some individual link, will be given by (1). But the probability for the next step, namely that the next link is left unattacked is now given by

$$\frac{n-r}{n-1} = (1 - \alpha) \left( 1 + \frac{1}{n} + \dots \right)$$

as now only  $(n - 1)$  links are available to be split, while at the beginning of the whole process  $n$  were present. If, of course,  $n$  is infinitely large, we can replace  $(n - 1)$  by  $n$ . Then we come back to the Kuhn and Flory formula.

Continuing in this way, the probability that the next and succeeding bonds remain intact is:

$$\frac{n-r-1}{n-2}, \quad \frac{n-r-2}{n-3},$$

and so on.

Finally, the last step of cutting out a shorter chain from a longer one, namely that at the end of a chain with  $s$  links again one bond is opened will be represented by

$$\frac{r-1}{n-s-1}.$$

We have now, according to Simha, calculated all the individual probabilities of the single elementary steps which take place if one cuts out a chain of  $s$  links from an original chain with  $n$  bonds. To get the

total probability we have again to multiply the elementary ones and get

$$w_s = \frac{r}{n} \left\{ \frac{n-r}{n-1} \cdot \frac{n-r-1}{n-2} \cdots \frac{n-r-s+1}{n-s} \right\} \frac{r-1}{n-s-1}. \quad (3)$$

This equation expresses the fact that it is impossible to obtain a chain consisting of a number of linkages  $s$  greater than  $(n-r)$ .

If we now want to find out all possible chains with  $s$  links which can be cut out of a chain with  $n$  bonds, we apparently have to multiply the expression by the factor  $(n-s-1)$ . This means only that in producing  $s$ -membered chains we have to start at any individual bond of the original molecule, so long as the possibility of having an  $s$ -membered chain is still present. This leads us to the relation

$$W_s = (n-s-1)w_s \quad (4)$$

which gives the total probability for getting chains with  $s$  links.

To compare these considerations with experimental fractionation results we have to find the total number of monomeric molecules which are embodied in chains of a given length  $s$ . This number, as a function of chain length, would give us the distribution curve of the molecular weight fractions as defined by Carothers and Flory.<sup>5</sup>

As a chain of  $s$  links contains  $(s+1)$  monomeric molecules, the total number of ground molecules comprised in chains with  $s$  links will be given by

$$Z(s, n, r) = \frac{r}{n} (r+1) \frac{(n-r)!}{(n-1)!} \frac{(n-s-1)!}{(n-r-s)!} \cdot (s+1). \quad (5)$$

This equation evidently allows to calculate the distribution curve of the molecular weight fractions at any given degree of decomposition  $r$  if the length  $n$  of the original chains is known. Putting  $n \gg s$ ,  $n-r \gg s$ ,  $r \gg 1$ , we again neglect the influence of the original chain length and return to the formula (2) of Kuhn and Flory.

Each distribution curve represented by equation (5) gives  $Z$  as a function of  $s$ , when  $n$  and  $r$  are given. It offers, therefore, an immediate possibility for a direct comparison with experiment if during a decomposition reaction of a long chain compound at different stages of the degradation distribution curves have been measured.<sup>7</sup>

## 2. Degradation Experiments and their Comparison with the Theory.

In recent years several attempts have been made to follow the course of a polymerisation reaction, not only as to the total amount of polymerised matter, but also as to the distribution curve of the material which

<sup>7</sup> The derivation described above neglects two further ways of obtaining fragments of the length  $s$ . First, the possibility of cutting out simultaneously 2, 3 . . .  $q$  fragments if  $r > 2$  and  $n \geq qs$ , and secondly the possibility of getting segments one end of which coincides with one end of the original chain. It can be seen, however, that the probability for the first case is of a lower order of magnitude than that given by (3) and (4). The second possibility is taken into account by introducing the factor  $(r+1)$  in (5) instead of  $(r-1)$  in (3). It is further assumed that the value of  $r$  is the same for all chains undergoing degradation, instead of considering that there will be a certain distribution of  $r$ -values. This refinement may be omitted, however, because the present state of our experimental knowledge would hardly allow a sufficient exact check of the formulae.

is present at different stages of polymerisation.<sup>8</sup> It seems to be of interest to carry out similar investigations on degradation reactions. This can be done if one secures as initial product a material of sufficient homogeneity and carries out the degradation under homogeneous and mild conditions. Then one takes out of the reaction mixture at different times samples sufficiently large to be analysed, not only in regard to their average degree of polymerisation but also so as to be divided into several fractions in order to find out their distribution curves.

A series of such experiments was started in 1935 in Vienna with the scope of a systematic analysis of different degradation reactions of high molecular compounds.

In the following we select only the results obtained by the acetolysis of cellulose acetate under conditions similar to those described by P. Karrer, M. Bergmann, K. Hess and their collaborators.<sup>9</sup>

As initial material there was chosen a technical sample of cellulose acetate produced under the name of "cellite." The analysis of the material showed that about  $2\frac{1}{2}$  hydroxyl groups per glucose unit were acetylated. The acetyl content was found to be 39.3 %. Pure cellulose triacetate contains 44.8 pure cellulose diacetate 34.8 % acetyl. The material was easily soluble in acetone and gave in very dilute solution (0.267 g. per l.) a specific viscosity of 0.099. According to the Staudinger equation this corresponds to a molecular weight of about 110,000. As characteristic constant for cellulose diacetate in acetone the value found by Obogi and Broda<sup>10</sup>

$$K_m = 9.0 \times 10^{-4}$$

was used. The degree of polymerisation of this sample is about 410.

The moisture of the material amounted to 5.4 %, its ash content was 0.12 %.

4000 g. of this technical material were first fractionated according to the method of H. J. Rocha<sup>11</sup> by dissolving in acetone and gradually precipitating the material with water. It has already been proven by Obogi and Broda that the fractions which can be obtained in this way are fairly homogeneous.

For further investigations a fraction of about 800 g. was selected which had an average polymerisation degree of about 350. This corresponds to a molecular weight of about 93,000 and to a specific viscosity of 0.084. All viscosities were measured at 25° C.

In order to get an idea about the homogeneity of this initial material a fractionation curve of it was worked out. Table I. and Fig. 1 contain the

TABLE I.—INITIAL SUBSTANCE;  $\bar{P}$  (DETERMINED DIRECTLY BY VISCOSITY MEASUREMENT) EQUAL 350.

Fraction 1	7 %	has $P = 270$	} average value $\bar{P} = 345$
" 2	82 %	has $P = 340$	
" 3	12 %	has $P = 400$	

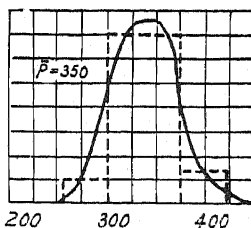


FIG. 1.

results. In all figures the degree of polymerisation is shown in the abscissæ, while the relative amount of material belonging to this polymerisation degree is on the ordinate. It can be seen that this starting

<sup>8</sup> Cf. e.g. W. J. Breitenbach, *Mh. Chem.*, 1938, **71**, 721; H. W. Melville, *Trans. Faraday Soc.*, 1935, **32**, 315.

<sup>9</sup> P. Karrer and P. Widmer, *Helv.*, 1921, **4**, 174; M. Bergmann and E. Knehe *Ann.*, 1925, **445**, 1; W. Weltzien and R. Singer, *ibid.*, **443**, 71; K. Hess and H. Friese, *ibid.*, 1926, **450**, 40; M. Bergmann and H. Machemer, *Ber.*, 1930, **63**, 316; K. Hess and M. Ulmann, *Ann.*, 1937, **498**, 77.

<sup>10</sup> R. Obogi and E. Broda, *Kolloid Z.*, 1934, **69**, 172.

<sup>11</sup> H. J. Rocha, *Kolloid Bh.*, 1930, **30**, 230; cf. also R. O. Herzog and A. Deripasco, *Cell. Chem.*, 1932, **13**, 25; W. Herz, *ibid.*, 1934, **15**, 95.

material was, as a matter of fact, a fairly homogeneous product; 82 % of it showed an average polymerisation degree of 340, only 7 % were below and 12 % above. Fig. 1 shows a graphical interpretation of these results. The experimentally obtained fractions are plotted in dotted sharp-edged lines. One sees that two small fractions are situated on each side of the main fraction. This discontinuous distribution corresponds to the actual experimental procedure. The total amount of the material is represented by an area which corresponds to 25 small squares.

As can be seen from the figure, the width of the main fraction has been assumed to be larger than the width of the two side fractions. This corresponds to the fact that if one precipitates a large amount from a colloidal solution considerable fractions of a material which should stay in solution is taken out together with the precipitating substance. Obogi and Broda, and later H. Lachs and Douglas and Stoops,<sup>12</sup> discovered that such effects can falsify the shape of a distribution curve quite considerably.

In our case it was proved experimentally by a second fractionation that the main fraction was considerably wider than the two side fractions.

In addition to the directly measured fractionation results, a smooth curve is drawn in Fig. 1, which represents as well as possible the actual distribution curve of the material. If one calculates the average degree of polymerisation from the fractionation experiment one gets 345 while the direct measurement gives, with the aid of Staudinger's equation, the

TABLE II.—RESULTS OF FRACTIONATION AFTER DIFFERENT REACTION TIMES.

Degradation Product.	$\bar{P}$ .	$r$ .	$\alpha$ .	Fractionation Results.				
1	158	1.2	0.0034	17% 64,	24% 114,	26% 167,	22% 206,	11% 300
2	100	2.5	0.0071	12% 24,	26% 51,	36% 98,	18% 163,	8% 236
3	54	5.5	0.0157	13% 10,	18% 44,	52% 53,	15% 95,	2% 180
4	31	10.3	0.0294	14% 14,	68% 27,	14% 60,	4% 75	

value of 350. Considering the approximate character of the Staudinger equation and the experimental difficulties in getting precise values for the viscosity this agreement may be regarded as fairly satisfactory.

This material was then slowly degraded by dissolving it in a mixture of acetic anhydride and acetic acid. As the substance dissolves in this mixture and the acetolysis takes place in this solution one may feel entitled to regard this reaction as being sufficiently homogeneous to apply the above mentioned formulæ which are derived from purely statistical considerations and therefore only hold for homogeneous reactions. After 24 hours, one quarter of the total mixture was removed from the reaction vessel, the solution was diluted with water, and the degradation interrupted in this way. The cellulose acetate was precipitated during the addition of water and separated from the liquid. Then this fraction was washed properly and dried, and in this state it was ready for a determination of its average molecular weight and for further fractionation.

This fractionation was carried out as described above, following the procedure elaborated by H. J. Rocha, Obogi and Broda, E. W. Mardless and H. Lachs.

The first line in Table II. shows the result of these measurements. In the first column we find the number of the degradation product, in the second the average degree of polymerisation as observed by direct viscosity

<sup>12</sup> R. Obogi and E. Broda, *loc. cit.*<sup>9</sup>; H. Lachs, J. Kronman and J. Wajs, *Kolloid Z.*, 1937, 79, 91; 1938, 84, 199; 1939, 87, 195; cf. also E. W. Mardles, *ibid.*, 1939, 49, 4; I. D. Douglas and W. N. Stoops, *Ind. Eng. Chem.*, 1936, 28, 1152.

measurement, and in the third and fourth columns the theoretical evaluation of these experiments, which will be discussed later. The last column gives the result of the fractionation.

From this table one can see that the first degradation product has an average degree of polymerisation of 158, which means that on the average every chain has been cut into about two parts. The fractionation of this product shows that a very inhomogeneous mixture prevails in this state of degradation. The different fractions reaching from a degree of polymerisation of about 60 to about 300 do not vary very much in their relative amounts. There is a very smooth maximum around 160 which obviously corresponds to the mean polymerisation degree of 158.

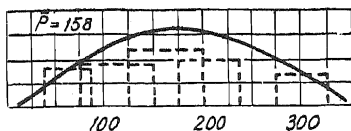


FIG. 2a.

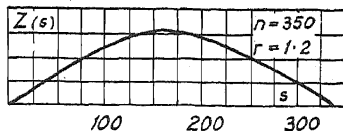


FIG. 2b.

Fig. 2a shows in dotted sharp-edged lines the direct result of the experimental fractionation which has been transformed into a smooth distribution curve following the same procedure as described above in Fig. 1.

In order to compare these results with the requirements of equation (5) we have to choose appropriate values for  $n$  and  $r$  and then calculate  $Z(s)$  as a function of  $s$ . Obviously for  $n$  we have to take the original average degree of polymerisation, namely 350. To get the value of  $r$  we take the average degree of polymerisation of the first degradation product, which is around 160. To obtain such a degree of degradation it is obviously necessary to cut each chain of the original material between 1 and 2 times. If there were an entirely homogeneous starting material with  $n = 350$  and each chain were cut once, then we should get a degradation product with

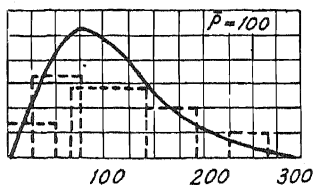


FIG. 3a.

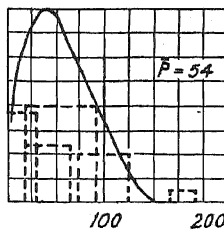


FIG. 4a.

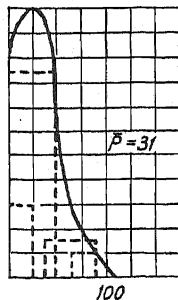


FIG. 5a.

the chain length 175; if it were cut twice about 120. Hence the degradation product of a degree of polymerisation 158 has undergone between 1 and 2 cuts in every chain, on the average 1.2. If we introduce this into equation (5) and calculate the distribution curve we get as a result the curve shown in Fig. 2b. The measure in this figure was again chosen in such a way that 100 % of the investigated material is represented by 25 small squares. One sees that equation (5) gives also a very broad distribution curve at this low degree of degradation, a curve which corresponds to a fair extent to the experimental one.

In the same way, three more degradation products were removed from the reaction mixture, precipitated and analysed. The results of the fractionation experiments can be seen in Table II.

It is quite obvious from these figures, that the further the degradation proceeds the sharper the distribution curve gets. This can be seen still better in Figs. 3a, 4a and 5a. They are all drawn under the conditions which have been described above and show clearly the steady accumulation of higher degraded substances as the reaction time goes on.

Figs. 3b, 4b and 5b show the respective theoretical distribution curves calculated in the above-mentioned manner.

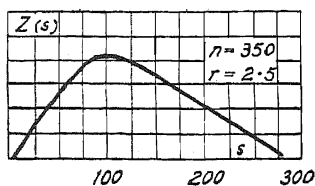


FIG. 3b.

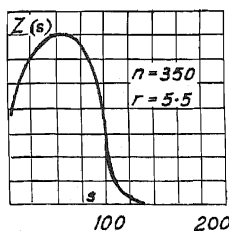


FIG. 4b.

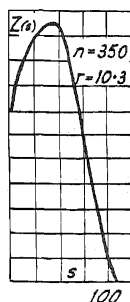


FIG. 5b.

Although there is no complete quantitative agreement between the experimental and theoretical curves, they show a very good general concordance; equation (5) is certainly capable of following the results of the experimental work reasonably well. This means, of course, no more than that the conditions assumed during the derivation of this equation, namely a prevailing homogeneity in the reacting system, have been sufficiently fulfilled.

### Summary.\*

1. Degradation experiments have been carried out with cellulose acetate of improved uniformity and the distribution curves of the degradation products at four different stages of the reaction have been investigated.
2. The results obtained have been compared with a statistical equation worked out for the degradation of long chain molecules following the theory of Kuhn and Flory.
3. The comparison between the theoretical and experimental results gave at least a qualitative agreement between them.

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\* A more detailed derivation of a general degradation formula on the basis of a more complete theory will be given elsewhere. Compare in this respect footnote 7.

# SOLUBILITY AND SWELLING OF HIGH POLYMERS IN TERNARY MIXTURES.

BY J. N. BRØNSTED AND K. VOLQVARTZ.

*Received 12th January, 1940.*

In systems composed of a high polymer and a liquid medium of normal molecular weight the occurrence of three different kinds of equilibria may be anticipated.<sup>1</sup> The liquid may be a *non-solvent* (N), in which case no sort of interaction between the two components takes place. It may be a *solvent* (S), in which case the two components will mix in all proportions. Finally the liquid may be a *swelling medium* (Sw). This means that the high polymer phase takes up liquid to form a "swelled phase" of a fixed composition, while the "liquid phase" consists of the pure medium only, containing no trace of the polymer.

The fourth case conceivable, in which the high polymer shows some solubility in the liquid medium while at the same time swelling is absent, does not seem to exist. In other words, the anomalous behaviour of a high polymer is associated with its function as a solute rather than as a solvent. The sharp distinction between the various liquids as regards their effect upon a high polymer is, therefore, to be found between Sw and S rather than between N and Sw.

In a three-component system where the high polymer is in equilibrium with a mixed medium, a variety of phenomena depending upon the type of the mixture are to be expected. Using the classification of media as N-, Sw- and S- media a total number of six types of mixtures are possible, two of which, however, show no special characteristics other than two-component systems. The remaining four types are:—

In all cases when an S- medium enters as one of the components, or when a mixture acts as a solvent (see below), the interesting *critical* phenomena previously described are bound to appear.

The present work deals with the study of such three-component systems using polystyrene as the high polymer.

For experimental determination of the equilibrium in case the swelling does not exceed 80 or 90 %, polystyrene covering the inside of a small bulb as a thin film was rotated with the binary medium at constant temperature (20°). Sw and S present in the mixture then to some extent penetrate into the film to form a solution in it. Also a non-solvent, however, which is inactive towards the pure film, will dissolve more or less when the film has taken up Sw or S, in which N is soluble. Finally, therefore, in all cases a two-phase equilibrium is reached in which one phase is a *binary* liquid medium and the other a *ternary* swelling phase.

Designation.	Type of Medium.	Number of Systems, Investigated.
I	N—Sw	1
II	N—S	4
III	Sw—Sw	3
IV	Sw—S	4

<sup>1</sup> Brønsted, *C. r. Lab. Carlsberg, Sér. chim.*, 1938, **22**, 99.



Thus using a mixture of ethyl alcohol and benzene, the first thing to happen is swelling of the film due to benzene being dissolved. As this process proceeds, the ethyl alcohol also, which in a pure state is a non-solvent, to some extent passes into the film until a state of equilibrium is reached in which both of the two liquid components are present in both phases.

The amount of liquid being used in an experiment of the type described here was always so large compared with the amount of polymer

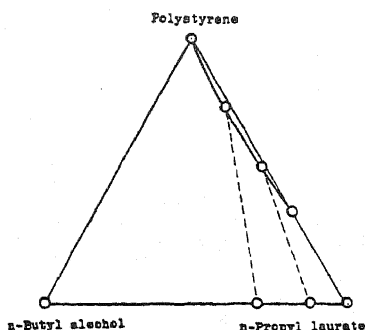


FIG. 1.

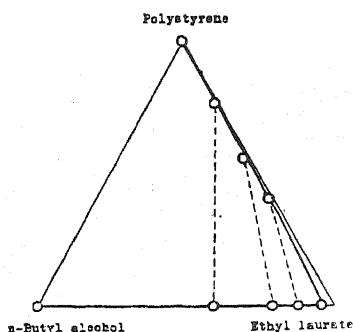


FIG. 2.

that either no measurable change in the composition was caused by the swelling, or at any rate only such a change as could easily be corrected for. An analysis of the liquid phase after establishment of the equilibrium was therefore not necessary. For the determination of the total amount of liquid taken up by the film the same methods were used as previously described<sup>2</sup> in the case of a single medium. Analysis of the dissolved mixture, however, is not easy unless the two liquids can be

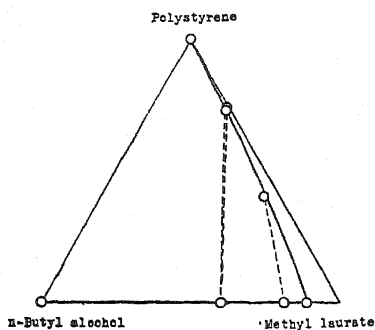


FIG. 3.

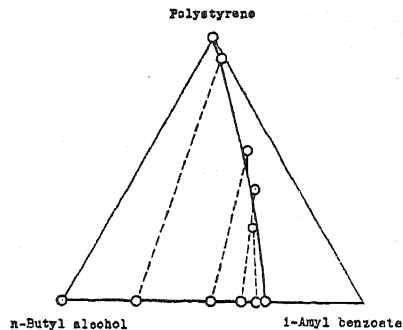


FIG. 4.

separated by evaporation. Therefore in nearly all experiments components of widely different volatility were chosen for the liquid medium. The more volatile liquid was evaporated in a current of air until approximately constant weight, whereafter the less volatile component was evaporated at higher temperature.

In the case of the ethyl laurate-propyl laurate mixture a different method was adopted. The liquid mixture was separated from the film

<sup>2</sup> Brønsted and Volqvartz, *Trans. Faraday Soc.*, 1939, **35**, 576.

by vacuum distillation, and in the distillate—amounting only to a fraction of a cubic centimetre—the composition was determined by determining its critical temperature towards a certain preparation of polystyrene which was calibrated against synthetic mixtures of the two esters. This method is very suitable for the purpose, since the critical temperatures for the two esters in a pure state differ by about  $30^{\circ}$ .

The results are presented in the accompanying triangular equilibrium diagrams in which a point represents the weight fractions of the three

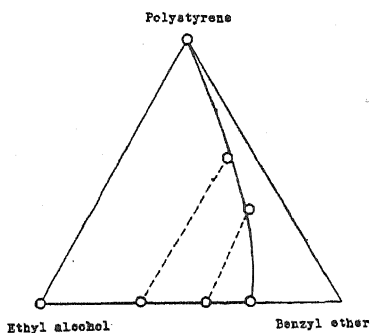


FIG. 5.

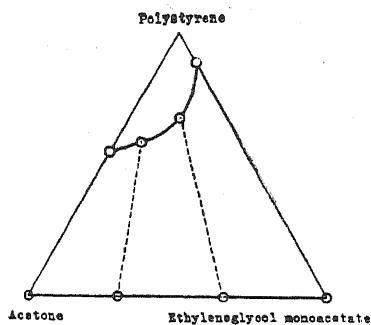


FIG. 6.

components. Conjugate points, *i.e.* points representing phases in equilibrium, are combined by dotted lines.

The accuracy of the results varies somewhat from case to case. The diameter of the circles in the figures may present the average error in the case of a swelling amounting to 50 % or more. If the polymer takes up only little of the medium the process of swelling is considerably slowed down and the error is likely to be larger.

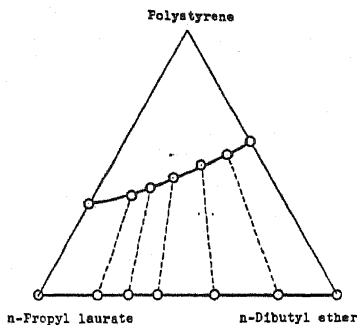


FIG. 7.

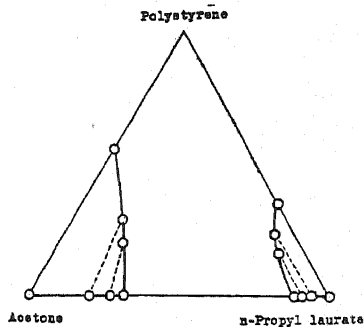


FIG. 8.

The end points of the swelling curve on the ground line are "critical" points. They were determined in 0.1 % solutions of polystyrene in S by addition of N or Sw until appearance of a certain very faint degree of turbidity. The corresponding composition of the medium is given in the figure as *critical points*.

Fig. 1 shows an equilibrium of type I involving butyl alcohol as a non-solvent and propyl laurate as a swelling medium. The saturation point in the binary polystyrene-propyl laurate system lies—as found in the previous investigation—at 64 % laurate. Addition of butyl alcohol

to the liquid medium causes a rapid decrease in the swelling, so that almost the whole area of the diagram shows the state of heterogeneity.

Exchanging ethyl or methyl laurate for the propyl ester the diagram changes into type II. Picturing this change as being a continuous process one may imagine the "saturation point" to pass gradually down the side axis of the triangle into somewhere in the ground line where it becomes a critical point. The same type is shown by mixtures of other esters with alcohols as for instance those presented in Figs. 4-5.

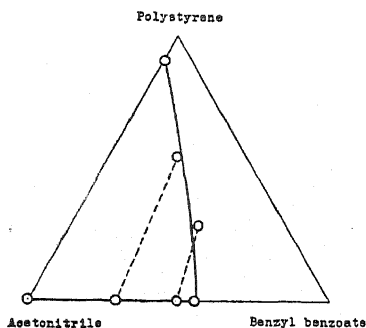


FIG. 9.

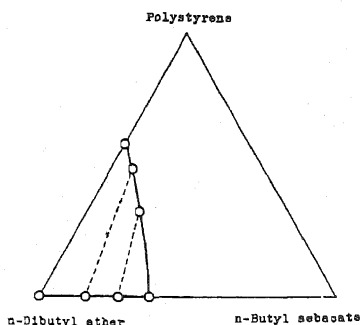


FIG. 10.

Type III, comprising two swelling media, is presented by the ethylene-glycol monoacetate-acetone and the propyl laurate-butyl ether systems, shown in Figs. 6 and 7. These two systems show the normal behaviour of media of this type. There is, however, another possibility pertaining to type III and presented by the propyl laurate-acetone mixtures of Fig. 8. From the shape of the curves in this diagram we see that continuous addition of one of the components to mixtures having the other component in excess causes such a large increase in the swelling of the

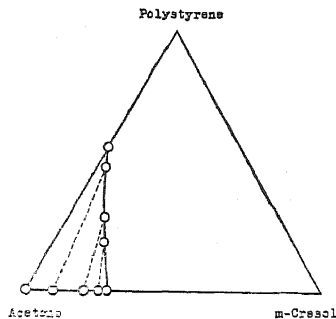


FIG. 11.

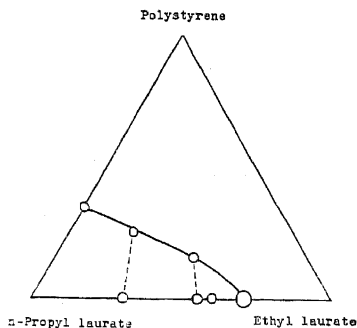


FIG. 12.

polymer that finally a region is reached in which the mixture has become a solvent. The swelling curve then falls into two separate branches each cutting the ground line in a critical point. Obviously from a solution within the interval between these critical points a swelled phase may be precipitated by addition of either of the two pure media. Thus a 50 % mixture is miscible with polystyrene in all proportions. Addition of a certain amount either of acetone or of the ester precipitates a swelled phase.

Figs. 9-12 finally show cases of type IV. Special interest is associated with the system propyl laurate-ethyl laurate on account of the great chemical similarity between the two media. In spite of their similarity they belong at ordinary temperature to different solvent types, but as shown in the previous paper this difference may disappear on change of temperature.

The polystyrene used in these experiments was prepared by polymerization of pure styrene at ordinary temperature and repeated reprecipitation from benzene-ethyl alcohol mixtures. By this procedure, the effect of which can be followed by viscosity measurements, the low molecular material preferably remains in solution while the high molecular material accumulates in the precipitate.

To show the effect of this method the following details of an experiment are given: 23.0 g. of the polymerized material was dissolved in 2 l. of benzene and partly precipitated with 900 c.c. of absolute ethyl alcohol in a thermostat at 22°. The precipitate, which appears as a jelly, after drying was treated in a similar way, and so forth until the residue left was only 0.2 g. Table I gives the weight of the various fractions and the *viscosity constant* of the corresponding benzene solution at 20° expressed as

$$\frac{1}{x} \cdot \frac{\eta - \eta_0}{\eta_0},$$

where  $\eta_0$  is the viscosity of the solvent (benzene),  $\eta$  the viscosity of a dilute solution usually containing 0.1 % of the polymer, and  $x$  the weight fraction of the polymer in the solution. This constant is a modification of Staudinger's specific viscosity

$$\frac{1}{c} \cdot \frac{\eta - \eta_0}{\eta_0},$$

where  $c$  is the "basic molality."<sup>3</sup> The relation between  $x$  and  $c$  is

$$x = c \frac{G}{1000 d},$$

where  $G$  is the basic molecular weight (= 104 for polystyrene) and  $d$  the density of the solvent.

As seen from this table further fractionation beyond Fraction F has little effect. These fractions have a viscosity constant about one and a half times as large as the high-molecular material reported by Staudinger.<sup>4</sup> We have obtained some evidence to substantiate the finding of this author that the very high-molecular polystyrene is unstable.

The molecular weight of the polymer is of no significance for the degree of swelling if the equilibrium point is not too close to the ground line. For most experiments, therefore, material having a viscosity coefficient between 500 and 800 was sufficient. For the determination of the critical points, however, the most high-molecular preparation was used, since the critical phenomena—as previously explained—are bound to occur only when such material is employed. Even Fraction I does not fulfil the requirements for an unequivocal proof of the critical phenomenon. This is particularly true in the case of the laurate ester mixtures, and the position of the critical point in this case is therefore particularly uncertain.

TABLE I

Fraction.	Weight	Viscosity Constant.
A	23.3	405
B	18.0	730
C	5.5	970
D	2.7	—
E	1.80	1340
F	1.57	1450
G	0.95	1440
H	0.60	1410
I	0.20	1523

<sup>3</sup> H. Staudinger, *Die hochmolekularen organischen Verbindungen*, 1932, 155, 56.

<sup>4</sup> Staudinger, *loc. cit.*,<sup>3</sup> 189.

### Summary.

The equilibrium in ternary systems containing polystyrene has been determined. As in binary mixtures one phase in the equilibrium is a swelled phase while the other consists of the pure medium. The experiments are compatible with the existence of ternary critical points.

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## A NOTE ON THE CORRELATION OF UPPER ELECTRONIC STATES OF HOMOLOGOUS MOLECULES.

By R. F. BARROW.

*Received 13th February, 1940.*

In a recent series of investigations,<sup>1, 2, 3, 4, 5</sup> on the diatomic molecules MX, where M and X are Group-IV(b) and Group-VI(b) atoms respectively, the variation of the electronic and vibrational constants among the members of this group of homologous molecules has been considered in some detail. Examination of the behaviour of these constants among the Sn and Pb compounds is complicated by the fact that they have been postulated to possess from three to five upper electronic states, whose theoretical types are for the most part unknown, and which are only determinable with difficulty, since in these heavy molecules the band-origins lie very close to the respective band-heads.

In a group of similar molecules, the vibration frequencies of corresponding states exhibit a large mass effect, which is expressed in the general regularity of the curves of (a)  $1/\omega_e$  against  $n$ ,<sup>2, 5</sup> (b)  $\log(\omega_e)$  or  $1/\omega_e$  against  $\log(\mu)$ , in the group mentioned above, and (c)  $\omega_e$  against  $\mu^{1/2}$ , as observed in the group of halogen molecules and metallic halides. Derived functions of  $\omega_e$  have been suggested as possible grounds for the classification of excited states,<sup>7</sup> but it was later shown that some caution must be used in this application,<sup>4</sup> and it is also to be noted that  $\omega_e$  may be rather insensitive, being often nearly constant in a series of upper states of the same molecule.

Attention is therefore directed towards the other quantity which is accurately determined from vibrational analysis, namely the electronic energy,  $v_e$ . The close proportionality of this to the ionisation potentials of the atoms in the series of Group-II hydrides has been recognised for some time,<sup>1</sup> and in a later paper,<sup>4</sup> the upper states of the compounds of Sn and Pb with Group-VI(b) atoms were tentatively correlated on the basis of the assumption that the ratio of the electronic energies of comparable upper states to the product of the atomic ionisation potentials was constant.

<sup>1</sup> W. Jevons, L. A. Bashford, and H. V. A. Briscoe, *Proc. Physic. Soc.*, 1937, 49, 543.

<sup>2</sup> R. F. Barrow and W. Jevons, *Proc. Roy. Soc. A*, 1938, 169, 45.

<sup>3</sup> R. F. Barrow, *Proc. Physic. Soc.*, 1939, 51, 267.

<sup>4</sup> R. F. Barrow, forthcoming paper on SnTe, *Proc. Physic. Soc.*, 1940, 52, iii.

<sup>5</sup> R. F. Barrow and W. Jevons, forthcoming paper on GeSe and GeTe.

<sup>6</sup> A. Carrelli and P. Trauttsur, *Nuovo Cim.*, 1937, 14, 301.

<sup>7</sup> H. G. Howell, *Proc. Roy. Soc. A*, 1936, 153, 683.

It is the object of the present note to draw attention to the variation of  $I_1 I_2$  with  $\nu_e$  in a further group, the alkali metal molecules. In Fig. 1 values of  $(I_1 I_2)^{\frac{1}{2}}$  are plotted as ordinates against  $\nu_e$  as abscissæ. It is apparent that the points are grouped quite closely about straight lines. The significant fact is that these lines relate upper electronic states of different molecules, which are, so far as they have yet been determined by examination of their rotational structure, of the same theoretical type. Thus points grouped about II relate to  $^1\Sigma$  states, about VI to  $^1\Pi$  states. The correlation is not, of course, precise, since the trends of the

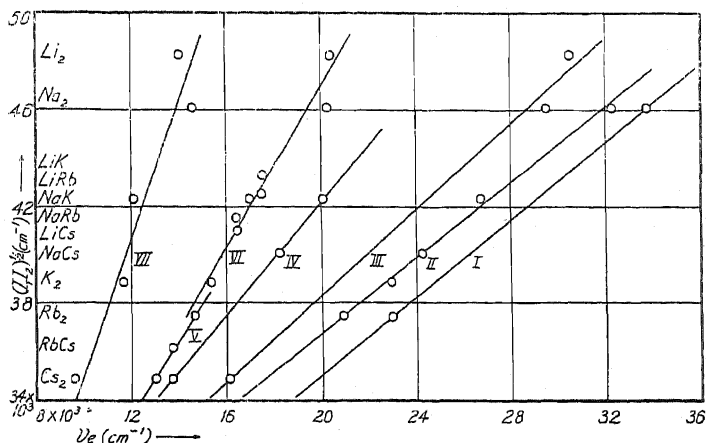


FIG. 1.— $(I_1 I_2)^{\frac{1}{2}}$  plotted against  $\nu_e$  for upper electronic states of the diatomic alkali metal molecules.

- In I,  $\text{Na}_2$  is known to be  $^1\Pi$ ,  
 II,  $\text{Na}_2$ ,  $\text{NaK}$ ,  $\text{K}_2$ ,  $\text{Rb}_2$  are known to be  $^1\Sigma$ ,  
 III,  $\text{Na}_2$  is known to be  $^2\Sigma$ ,  
 IV,  $\text{NaK}$  is known to be  $^1\Pi$ ,  
 V,  $\text{Rb}_2$  is known to be  $^1\Sigma$ ,  
 VI,  $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{NaK}$ ,  $\text{K}_2$  are known to be  $^1\Pi$ ,  
 VII, all are known to be  $^2\Sigma$ .

The remainder of the states are unknown.

$\nu_e$  data have been taken from Henri<sup>8</sup> and Jevons<sup>9</sup>; ionisation potentials from Herzberg.<sup>10</sup>

primary ionisation potentials do not reflect exactly the changes in electronic binding as measured, for example, by the primary excitation energies. Nor is it suggested that there will prove to be a direct relation between  $(I_1 I_2)$  and  $\nu_e$  in all groups of homologous diatomic molecules, for, even where the relation exists, it may not be apparent in cases where the departures of the points from the straight lines are of the same order of magnitude as the separation of the states. Nevertheless, such regularities as do occur are not without interest, and may prove to be of some use in the classification of states the determination of whose theoretical type by rotational analysis is impracticable.

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 Oxford.

<sup>8</sup> V. Henri, *Tables Annuelles. Spectres Moleculaires*, 1ère Partie, Paris, 1937.

<sup>9</sup> W. Jevons, "Report on Band Spectra of Diatomic Molecules," *Physic. Soc.*, 1932.

<sup>10</sup> G. Herzberg, *Atomic Spectra and Atomic Structure*, London and Glasgow, 1937.

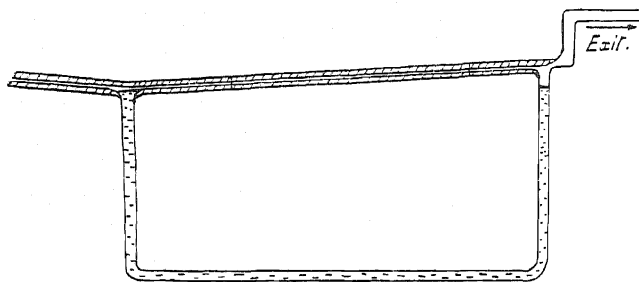
## A NEW TYPE OF FLOW METER FOR SLOW RATES OF FLOW.

By A. E. L. MARSH.

*A new type of flow meter is described which is independent of the viscosity of the gas for which it is used.*

*Received 27th March, 1940.*

During the course of some researches in this department, an instrument capable of measuring flow rates of the order of 1 to 0.25 c.c./min. was required. The differential manometer type is unsuitable over this range, and the instrument shown in the diagram was eventually designed.



The instrument was filled to the level shown with a suitable liquid such as amyl phthalate. The gas stream passing through the capillary pushed along a short thread of the liquid which, when it drained down the right-hand limb of the apparatus, pushed up a second bubble of liquid. On careful adjustment by tilting, it was found that the second bubble could be formed just as the preceding bubble reached the end of the capillary. This was probably due to a tendency for the liquid to drain back.

The volume of the capillary between the two etched graduations was previously determined and the flow rate was given directly by the time taken for the liquid thread to pass between the graduations.

The maximum bore of the capillary is limited by the above-mentioned tendency of the liquid to drain back. With amyl phthalate as the indicator liquid, capillaries up to 1 mm. bore were satisfactory.

The peculiar advantages of this instrument are its ease of construction and calibration, and its independence of the viscosity (and hence of the nature and temperature) of the gas for which it is used.

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# A NOTE ON THE BONDING POWERS OF GROUPS OF *d* ELECTRONS.

BY W. G. PENNEY.

Received 9th February, 1940.

The outstanding features of the bonding properties of *d* electrons have been discovered by Pauling,<sup>1</sup> using the simple criterion of maximum overlapping of wave functions in conjunction with the directional properties of atomic orbitals. Van Vleck<sup>2</sup> has explained how Pauling's results can be derived equally well from other approximations, such as those of molecular orbitals and the crystalline field potential. We shall now discuss a point which has previously been overlooked.

The ions  $\text{Ca}^{++}$ ,  $\text{Mn}^{++}$ , and  $\text{Zn}^{++}$  in aqueous solution, or in hydrated crystals, are in *S* states, while the other ions intermediate to them in the periodic table, are in *D* or *F* states. Now *S* states are not split up by crystalline forces, but *D* and *F* states are, the order of magnitude of the splittings being  $20,000 \text{ cm.}^{-1}$ . As a result, the ions in *S* states are not so closely bound to their water clusters as the other ions, the energy differences being about  $30 \text{ kcal./mol.}$

To estimate the differences in the binding energies of the various ions to their water clusters we envisage the following steps, shown diagrammatically in Fig. 1.

The initial system is the metal *M* in the solid state, together with a dilute acid solution, the amount of acid being just enough to form a divalent salt with the metal. Vaporise the metal, the energy of vaporisation being  $V \text{ kcal./mol.}$

Now form the ion  $\text{M}^{++}$ , the first and second ionisation potentials being  $I_1$  and  $I_2 \text{ kcal./mol.}$  respectively. The resulting two electrons per atom may be regarded as absorbed by two  $\text{H}^+$  ions in solution; the resulting normal atoms form a molecule and escape from the solution. Let the energy gained in this process be  $C \text{ kcal./mol.}$  The final state of the system is a dilute aqueous solution of the metallic salt, and from thermochemical measurements, let us say, is  $H \text{ kcal./mol.}$  more stable than the initial state. The heat of formation of the complex  $\text{M}^{++} \cdot 6\text{H}_2\text{O}$  from  $\text{M}^{++}$  and six water molecules is  $E$ , where

$$E = V + I_1 + I_2 - C + H.$$

The energy of the complex is  $-E$ , if the widely separated state is taken to be of zero energy.

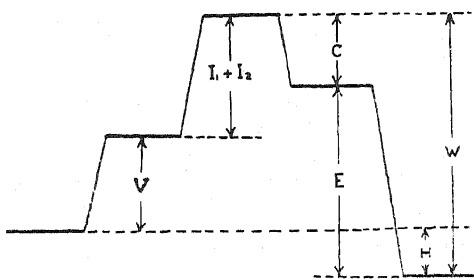


FIG. 1.

<sup>1</sup> Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

<sup>2</sup> Van Vleck, *J. Chem. Physics*, 1935, **3**, 803.



Since we are concerned only in variations in  $E$  from metal to metal, we may disregard  $C$  completely, and consider the energy  $-W$ , where

$$-W = V + I_1 + I_2 + H.$$

The quantity  $H$  may be taken either from thermochemical data on the heats of formation of dilute solutions of various salts, or more simply is given directly as the heat of formation of aqueous ions, the heat of formation of the aqueous hydrogen ion  $H^+$  (aq.) being taken arbitrarily as zero.

Our contention is that a plot of  $W$  against atomic number through the iron group sequence will show irregularities, Ca, Mn and Zn being about 30 kcal./mol less stable than the others. To test this, we clearly need the experimental values of  $V$ ,  $I_1$ ,  $I_2$  and  $H$ .

### The Heats of Vaporisation.

Probably the most accurate method of obtaining the heats of vaporisation of the iron group metals is from the slope of the  $\log p - T$  curve, where  $p$  is the vapour pressure at temperature  $T$ . Apart from Zn, the vapour pressure is not appreciable at temperatures ordinarily available. Apparently, no measurements of the vapour pressures of these metals have been made since 1914, and it is therefore not surprising that the values quoted in the literature for the heats of vaporisation vary widely. Grimm and Wolf<sup>3</sup> have made a critical examination of the published data. Sherman<sup>4</sup> and Bichowsky and Rossini<sup>5</sup> have recalculated most of the heats from the original data; and the latter authors have selected what, in their opinion, are the best values. Curiously enough, Bichowsky and Rossini do not mention the article of Grimm and Wolf. One may therefore compare the two sets of values and thus obtain an estimate of the probable errors. Table I gives in the first two rows the vaporisation energies of various iron group metals according to Grimm and Wolf and to Bichowsky and Rossini respectively. The units are kcal./mol.

TABLE I.

	Ca.	Cr.	Mn.	Fe.	Co.	Ni.	Cu.	Zn.
$V$ (Gand W)	39	83	63	108	105	101	76	32
$V$ (Band R)	48	88	74	94	85	85	81	27
$I_1$ . .	140	155	171	188	180	175	177	215
$I_2$ . .	272	382	361	371	397	418	465	412
$H$ . .	130	42	49	21	17	15	-15	36

Even for a metal as volatile as zinc there is a discrepancy of 5 kcal./mol., while for Ni and Co the discrepancy is as large as 20 kcal./mol. Measurements on Ca, quoted by Bichowsky and Rossini, were last made

<sup>3</sup> Grimm and Wolf, *Handbuch der Physik*, 1934, 24-2, 1073.

<sup>4</sup> Sherman, *Chem. Revs.*, 1932, 11, 94.

<sup>5</sup> Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, Reinhold, 1935.

in 1929, but even so, there is still a difference of opinion to the extent of 10 kcal./mol. There are no data on Ti, Sc and V.

If a plot of the above heats of sublimation is made, an irregular curve is obtained. The values jump up and down, and there can be no doubt that the true values do not lie on a simple smooth curve.

### The Ionisation Potentials.

Table I also gives the first and second ionisation potentials,  $I_1$  and  $I_2$ , taken from Bacher and Goudsmit.<sup>6</sup> In most cases, the values are accurate to about 1 kcal./mol. There is, however, some doubt concerning the value of  $I_1$  for Co, since it is obtained by a wide extrapolation of meagre spectroscopic data. Bacher and Goudsmit give "about 8.5 e.v.," but this value seems at least 0.5 e.v. too high, when compared

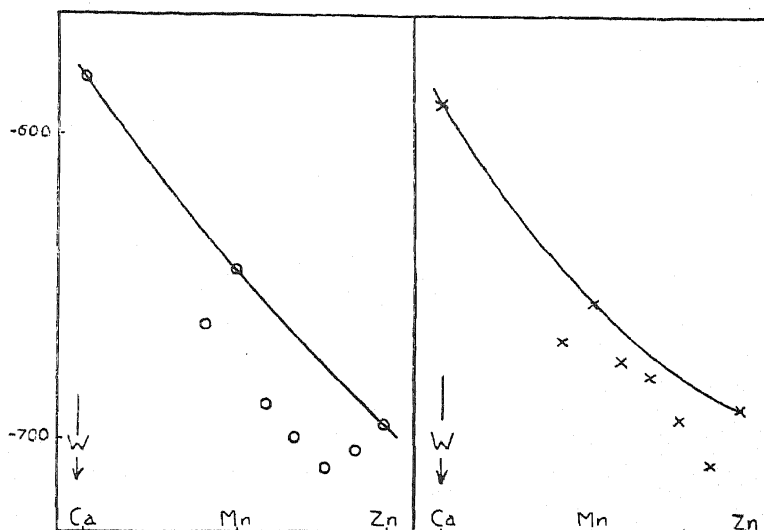


FIG. 2a and 2b.

with the other ionisation potentials. Bichowsky and Rossini have re-examined the data and give 7.8 e.v. This is the value we take.

### The Energies $H$ .

The last row of Table I gives the heats of formation of the aqueous ions, taken from the book of Bichowsky and Rossini.

### The Energies $W$ .

Figs. 2a and 2b show plots of the energies  $W$  defined by equation (2) above, against atomic number, the former being based on the heats of vaporisation given by Grimm and Wolf, and the latter on those of Bichowsky and Rossini. The two curves are parabolas drawn through the Ca, Mn and Zn points. In both diagrams the points for the other atoms lie well below the parabolas.

<sup>6</sup> Bacher and Goudsmit, *Atomic Energy States*, McGraw Hill, 1932.

We now investigate whether it is possible to apply corrections to the points representing the other atoms in such a way that they should now lie on the true parabola. Any substantial errors in the heats of vaporisation then show up immediately.

### Theory.

The stability of the cluster  $X^{++} \cdot 6H_2O$  is very largely governed by the attractive force of the positive double charge on  $X$  to the negatively charged oxygen atoms of the water molecules, and electrostatic Coulombic and exchange forces between the electrons of the various atoms in the cluster. The only electrons of  $X$  which need be considered are those in the shells  $3s$ ,  $3p$  and  $3d$ . The first two of these are full in every case; certainly their effective size varies, but only in a regular way through the sequence of ions  $X$ . We may therefore assume that the exchange and Coulomb interactions with the shells  $(3s)^2$  and  $(3p)^6$  varies steadily through the sequence. Similarly, the interactions between the water molecules vary but little, and even then, in a regular way.

Let us imagine that the  $d$  electrons in every  $X$  are averaged over a sphere. All of the above statements now apply to these  $d$  distributions. Actually, of course, the  $d$  electrons do not adopt an arrangement of spherical symmetry. The  $d$  electrons in certain of the  $X$  ions become oriented in such a way that their interaction energy with the water molecules is minimised, thus accounting for the extra stability of certain clusters, as shown in Figs. 2*a* and 2*b*. Only in three of the ions are the  $d$  electrons compelled to adopt a state of spherical symmetry, namely  $Ca^{++}$  which has no  $d$  electrons,  $Mn^{++}$  which has half a complete shell, and  $Zn^{++}$  which has a complete shell.

The variation of the interaction energies of various  $X^{++} \cdot 6H_2O$  clusters with the water molecules of the solution may be disregarded, since it is first small, and second regular.

From what has been said above, it is clear that we have now to calculate the differences in the energies of the most stable orientations of various groups of electrons  $d^0 \cdot d^{10}$  in the field of the water molecules, and the same configurations averaged over a sphere. The calculation is straightforward, and follows closely that developed by Penney and Schlapp.<sup>7</sup>

### The Crystalline Potential.

Theoretical studies of the magnetic properties of hydrated salts of iron group elements<sup>8</sup> have led to the conclusion that the motion of the  $d$  electrons are not seriously affected by the crystalline forces. Consequently, the effect of the crystalline forces on the  $d$  electrons may be regarded as a perturbation, most conveniently represented as a Taylor's series in the electronic co-ordinates  $x_i$ ,  $y_i$ ,  $z_i$ , referred to the centre of the ion as origin. Since the potential has cubic symmetry, it may be expressed in the form

$$V(x_i, y_i, z_i) = f(r_i) + D(x_i^4 + y_i^4 + z_i^4 - 3r_i^4/5) + E(x_i^6 + \dots) + \dots,$$

or in other equivalent forms.

The energy levels of the free ion are well described by the Russell-Saunders scheme. The effect of  $V$  is to disrupt the magnetic coupling of  $L$  and  $S$ , but is not sufficient to spoil the significance of  $L$  and  $S$ . In

<sup>7</sup> Penney and Schlapp, *Physic. Rev.*, 1932, 41, 194.

<sup>8</sup> Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, 1932.

other words, the exchange and Coulomb interactions of the  $d$  electrons of the ion with the surrounding water molecules are of subsidiary importance to the exchange and Coulomb interactions between the  $d$  electrons themselves. If, therefore, the energy diagram of a free ion is drawn, neglecting the orbit-spin forces, then the effect of  $V$  may be shown as a splitting of the  $L$  levels, and the splittings of the lower  $L$  levels are small compared with the intervals between the  $L$  levels.

The potential  $V$  through the sequence  $\text{Ca}^{++} - \text{Zn}^{++}$  will vary, but not very much. We assume that it is constant. The effect of  $V$  on a  $d$  electron varies with  $r^4$ , taken over the orbit. We neglect any variation throughout the sequence.

The term  $f(r)$  in  $V$  has no orienting effect on  $d$  electrons; the sixth-order and higher terms have no effect at all. The only term remaining is the fourth-order one.

TABLE II.

Ion.	State.	$\Gamma_1$ .	$\Gamma_3$ .	$\Gamma_4$ .	$\Gamma_5$ .	$\Delta$ .
$\text{Ca}^{++}$	$d^0 {}^1S$	0	—	—	—	0
$\text{Sc}^{++}$	$d^1 {}^2D$	—	12	—	-8	8
$\text{Ti}^{++}$	$d^2 {}^3F$	24	—	-12	4	12
$\text{V}^{++}$	$d^3 {}^4F$	-24	—	12	-4	24
$\text{Cr}^{++}$	$d^4 {}^5D$	—	-12	—	8	12
$\text{Mn}^{++}$	$d^5 {}^6S$	0	—	—	—	0
$\text{Fe}^{++}$	$d^6 {}^5D$	—	12	—	-8	8
$\text{Co}^{++}$	$d^7 {}^4F$	24	—	-12	4	12
$\text{Ni}^{++}$	$d^8 {}^3F$	-24	—	12	-4	24
$\text{Cu}^{++}$	$d^9 {}^2D$	—	-12	—	8	12
$\text{Zn}^{++}$	$d^{10} {}^1S$	0	—	—	—	0

Table II gives the effect of the potential  $D(x^4 + y^4 + z^4 - 3r^4/5)$  on the various ions  $\text{Ca}^{++} - \text{Zn}^{++}$ . The first column gives the ion; the next its electronic state when free. The next group of columns gives the decomposition of the lowest  $L$  state under the action of the field, the notation being that of Bethe.<sup>9</sup> Levels belonging to symmetry types  $\Gamma_1$  and  $\Gamma_2$  are singlets, to  $\Gamma_3$  are doublets, and to  $\Gamma_4$  and  $\Gamma_5$  are triplets (actually  $\Gamma_2$  does not appear). The units of energy  $\lambda$  is given in terms of the constants of the ion and the crystalline field by the equation

$$\lambda = \overline{r^4}D/105.$$

The last column in Table II is the most interesting one from our present point of view. It gives  $\Delta$ , the energy interval between the lowest level and the average position of all the levels. Since we have, in fact, chosen the origin of energy of the levels in each case to be the mean position,  $\Delta$  is simply the negative of the lowest energy level.

<sup>9</sup> Bethe, *Ann. Physik*, 1929, 3, 133.

A numerical value for  $\lambda$  may be had from work on the paramagnetic properties of the ions. Only in two cases are data available. According to Schlapp and Penney,<sup>10</sup> the overall separation of the level  $^3F$  of  $Ni^{++}$ , due to the crystalline field of an octahedron of water molecules, is about  $26,000\text{ cm}^{-1}$ . Krishnan and Mookherji,<sup>11</sup> using the equations of Schlapp and Penney, find a smaller value  $23,000\text{ cm}^{-1}$ , for a number of hydrated crystals of  $Ni^{++}$ . Becquerel and Opechowski,<sup>12</sup> from calculations on the paramagnetic rotation of nickel salts, obtain a splitting  $19,200\text{ cm}^{-1}$ . Since, in every case, the crystalline potential is determined from the deviations of the magnetic properties from "spin only" values, and these are quite small, the agreement is fairly satisfactory.

Jordahl<sup>13</sup> estimates  $19,000\text{ cm}^{-1}$  as the overall separation of the  $^2D$  level of  $Cu^{++}$  due to an octahedron of water molecules. The calculations are particularly difficult in this case because a non-degenerate orbital level is lowest.

If the assumptions on which Table II are based are valid, the ratio of the overall separations in  $Ni^{++}$  and  $Cu^{++}$  is 9:5. The separations given above do not fit this closely; but if we take the separation for  $Cu^{++}$  as  $14,000\text{ cm}^{-1}$ , and for  $Ni^{++}$  as  $21,000\text{ cm}^{-1}$ , the discrepancies are not large. Unfortunately the present thermo-chemical data are so discordant that they are of little use for refinements of these values. The corresponding value of  $\lambda$  is  $700\text{ cm}^{-1}$ , or  $1.98\text{ kcal./mol.}$

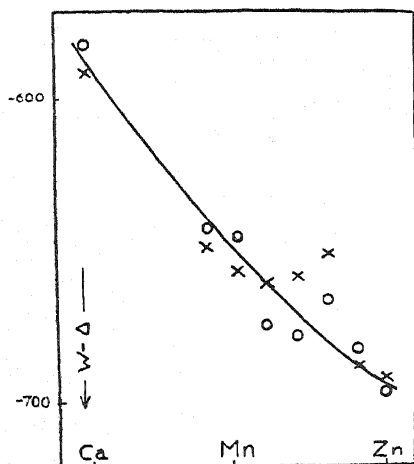


Fig. 3.

Evaluating the various quantities  $\Delta$  with this value of  $\lambda$ , and adding them to the energies  $-W$  plotted in Figs. 2a and 2b, we have obtained results shown in Fig. 3. The circles are values of  $-W + \Delta$  obtained from Grimm and Wolf's figures for the heats of sublimation of the metals, and the crosses from the corresponding figures of Bichowsky and Rossini. It will be seen that the representative points, although very scattered, do lie approximately on a smooth curve of little curvature. We have sketched in such a curve; clearly the data are not worthy of anything more elaborate.

An interesting feature of the curve is the way in which circles and crosses are distributed on both sides. From a study of Fig. 3, and a consideration of the probable errors in the theory given here, we venture on the following values of the heats of vaporisation of the metals (kcal./mol.).

M	Cr	Mn	Fe	Co	Ni	Cu
V	80	70	95	100	110	80

<sup>10</sup> Schlapp and Penney, *Physic. Rev.*, 1932, **42**, 666.

<sup>11</sup> Krishnan and Mookherji, *Phil. Trans., A*, 1938, **237**, 135.

<sup>12</sup> Becquerel and Opechowski, *Physica*, 1939, **6**, 1039.

<sup>13</sup> Jordahl, *Physic. Rev.*, 1934, **45**, 87.

### Conclusion.

The theory developed above is clearly on the right lines. When more accurate data become available, the theory can be improved, for example, by allowing for the variation in the ionic radius throughout the series, and by including interaction with higher levels of the ions.

The writer wishes to express his thanks to Dr. Purcell for helpful discussion.

*Imperial College of Science.*

## ON THE CALCULATION OF IONIC HEAT CAPACITIES IN SOLUTION.

BY D. H. EVERETT AND C. A. COULSON.

*Received 12th March, 1940.*

### 1. Introduction.

The inadequacy of Born's simple expression

$$\Delta G = - z^2 e^2 / 2Dr \quad \dots \quad (1)$$

for the Gibbs' free energy of charging of an ion in solution, in terms of its radius ( $r$ ) and the dielectric constant of the solvent ( $D$ ), has become increasingly apparent in recent years.<sup>1</sup>

In general terms this has been ascribed to saturation of the dielectric near the ion and attempts have been made to calculate this effect on the basis of classical electrostatics.<sup>2</sup> The problem may also be considered from a molecular standpoint, when the saturation of the dielectric may be treated in terms of the orientation of the solvent molecules in the neighbourhood of the ion. In this way Bernal and Fowler<sup>3</sup> have calculated the heats of solution of ions in water, and the treatment has been extended to the entropy change of the solution process by Eley and Evans.<sup>4</sup> Qualitatively one of us has recently<sup>5</sup> used the conception of solvent molecule orientation and the consequent "freezing out" of certain rotational degrees of freedom to account for the magnitude of the decrease in heat capacity accompanying the ionisation of acids.

The present calculations are intended, in part, to justify this hypothesis by demonstrating that the forces exerted by an ion on a water molecule in close proximity to it are sufficiently great to reduce substantially the contribution to the heat capacity of the system from certain rotational degrees of freedom of the water molecule. They also indicate a possible approach to the more general problem of the calculation of ionic heat capacities.

We are here concerned with the rotations of water molecules immediately adjoining either a positive or a negative ion. In section 3

<sup>1</sup> Askew, Bullock, Smith, Tinkler, Gatty and Wolfenden, *J.C.S.*, 1934, 1368; also *cf.* ref. 2.

<sup>2</sup> (a) Webb, *J. Am. Chem. Soc.*, 1926, 48, 2589; (b) Ingold, *J. Chem. Soc.*, 1931, 2179.

<sup>3</sup> Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

<sup>4</sup> Eley and Evans, *Trans. Faraday Soc.*, 1938, 34, 1093.

<sup>5</sup> Everett and Wynne-Jones, *ibid.*, 1939, 35, 1380.

we analyse these rotations into components, and, using the specific model described below, we are able to determine the potential energy curve for each motion. By solution of the wave equation

$$\nabla^2\psi + \frac{8\pi^2I}{h^2}(E - V)\psi = 0 \quad (2)$$

we then calculate the quantised energy levels ( $E_n$ ) and hence also the partition function ( $f$ ), since

$$f = \sum_{n=0}^{n=\infty} e^{-E_n/kT}. \quad (3)$$

The contribution of this degree of freedom to the heat capacity of the system is then given by the usual formula

$$C_v = T \frac{\partial^2}{\partial T^2} (kT \ln f). \quad (4)$$

The quantity in which we are mainly interested is  $C_p$  and not  $C_v$ . The difference between these may be shown to be small for water

$$(C_p - C_v = 0.18 \text{ cal./mol. } ^\circ\text{C.})$$

and for our present purpose we have regarded equation (4) as giving the value of  $C_p$ .

We do not intend to effect a complete calculation of the heat capacity change accompanying ionisation, for the following reasons. Firstly, any such calculation involves the evaluation of the difference between the heat capacity of water molecules round an ion and those in pure water. At present the structure of liquid water is not sufficiently well known to admit of any accurate calculation of the latter quantity, although by making not unreasonable assumptions we may arrive at a rough estimate of it. Secondly, we have only considered in detail the rotations of the water molecules in the immediate neighbourhood of the ion. The ions will, however, influence the structure of the water at greater distances; and other quantities such as the free volume of the water molecules may be affected by the presence of ions.

## 2. Description of Model.

**The Water Molecule.**—The water molecule is known from spectroscopic evidence to be triangular and we have used as our model one closely resembling that of Bernal and Fowler.<sup>3</sup> The angle between the two O—H directions was taken to be  $120^\circ$ , the O—H distance 0.90 Å. and the radius of the molecule 1.38 Å. The charge ( $\epsilon'$ ) on each H atom was taken as 0.49  $\epsilon$  and on the O atom 0.98  $\epsilon$ . The centre of rotation for all rotations has been taken to be the centre of the negative charge, which is also the centre of the molecule: in this respect our model differs slightly from Bernal and Fowler's, where the centre of negative charge is not quite coincident with the O nucleus. However, for rough calculations such as those in this paper, this difference is without significance and the calculations are slightly simplified.

**The Distribution around a Dissolved Ion.**—Following Bernal and Fowler, we may describe liquid water (at least just above its melting-point) as consisting of groups of  $\text{H}_2\text{O}$  molecules, with a semi-crystalline structure whose boundaries are continuously changing, such that each

molecule tries to surround itself tetrahedrally with four other water molecules. The forces tending to create, and preserve, this tetrahedral arrangement are dipolar forces which are not very powerful and are only partly successful in overcoming the tendency to contract from the very open tetrahedral structure (typical of ice) to the close-packed structure (typical of monatomic liquids). Thus Morgan and Warren,<sup>6</sup> from X-ray analysis, consider that the number of nearest neighbours in pure water changes with temperature from 4.4 to 4.9 in the range 0-100° C.; in pure tetrahedral packing the number is, of course, exactly four. In liquid water, then, there are micro-crystals of very indefinite size, and a molecule can wander from one group to another (as it must do in the process of viscous flow). The molecules will have rotations, many of which will be restricted if the liquid contains permanent dipoles (as water does); however, the restrictions to pure rotation will, in general, not greatly affect the contribution to the specific heat. The condition for appreciable restriction to occur is that  $h\nu$  must be of the order of  $kT$ , where  $\nu$  is the frequency of the restricted rotation. We shall, however, return to this question again in Section 5.

When an ion is dissolved in water, however, the situation is different; for the forces between a net positive or negative charge and a water dipole are much stronger than between two water dipoles. As a result we shall expect a far greater degree of ordering in the first co-ordination shell immediately outside the ion, since these molecules will be under a more intense field and their quantised rotational energy levels will be considerably changed. The orienting effect of the central ion will extend outwards beyond the first co-ordination shell and in the second and third shells also there will be a change of heat capacity. However, the discussion of these outer shells is very complicated since we ought strictly to allow for the mutual interaction of oriented molecules in each shell. It is clearly impossible to solve the problem of the various rotations in any self-consistent manner if we discuss more than a few molecules at a time, so that for the present we shall suppose that the free energy changes accompanying restricted rotation in all shells beyond the first are given by Born's equation; it will be sufficient for our purposes to show that the restricted rotation of the molecules in the first shell alone gives a distinct contribution to the change of heat capacity.

We are thus led to consider the rotation of a water molecule at a fixed distance from either a positive or a negative ion. In view of the uncertainties of the proper value to take for the radius of the central ion, we have analysed the various motions in the cases of ions of 1 Å. and 2 Å. radius. We shall suppose that there are four water molecules oriented round each ion. This is not entirely in agreement with the work of Stewart<sup>7</sup> who has shown experimentally that the co-ordination number is about 4.9 in ionic solutions, thus making the structure more close-packed. If we take this value for the co-ordination number, then our values of  $\Delta C_p$  calculated below should be increased.

### 3. Analysis of Restricted Rotation of Water Molecules.

The rotations of a water molecule in the field of an ion may be most conveniently analysed in terms of three rotations about mutually perpendicular axes passing through the centre of the water molecule:—

<sup>6</sup> Morgan and Warren, *J. Chem. Physics*, 1938, 6, 666.

<sup>7</sup> Stewart, *ibid.*, 1939, 7, 869.



(a) an axis joining the centre of the water molecule to the centre of the ion ;

(b) an axis which, together with (a), defines the plane of the mean position of the water molecule ;

(c) an axis normal to the plane of the water molecule in its mean position (see Fig. 1).

The motion about axis (a) may be described as an axial spin, while those about (b) and (c) have been termed "librations." Eley and Evans have not distinguished between the two, but, as we shall see, they must

be treated separately. To differentiate between them we shall use the terms "libration I" and "libration II" to refer to rotations about axes (b) and (c) respectively. In each case it is necessary to consider separately the effects of positive and negative ions since they orient water molecules in different ways and consequently the axes defined above will be, relative to the water molecule, different for oppositely charged ions.

The moments of inertia about the

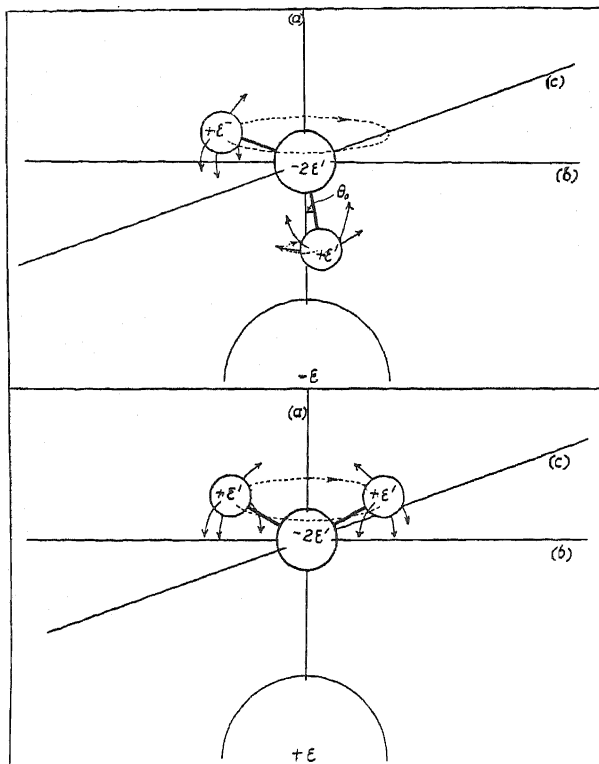


FIG. 1.—Rotational degrees of freedom of water molecule.

Top: Water molecule in field of negative ion.

Bottom: Water molecule in field of positive ion.

axes were taken to have the following values:—

$$\text{Orientation by negative ion: } I_b = 1.52 \times 10^{-40} \text{ g. cm.}^2$$

$$I_c = 2.70 \times 10^{-40} \text{ g. cm.}^2$$

$$\text{Orientation by positive ion: } I_b = 0.67 \times 10^{-40} \text{ g. cm.}^2$$

$$I_c = 2.70 \times 10^{-40} \text{ g. cm.}^2.$$

Most of the librations considered are governed by a potential that is effectively parabolic; thus

$$V = V_0 + \frac{1}{2} K \theta^2 \quad . \quad . \quad . \quad (5)$$

for small values of  $\theta$ , where  $\theta$  is the angle of displacement from the equilibrium position. The partition function for this is known to be

$$f = (1 - e^{-h\nu/kT})^{-1} \quad (6)$$

where  $\nu$  is the classical frequency of libration given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{I}} \quad (7)$$

in which  $I$  is the moment of inertia of the water molecule about the given axis of rotation. The contribution to the heat capacity is then given by

$$C_v = \frac{R}{2} \left( \frac{h\nu}{kT} \right)^2 \frac{1}{\cosh(h\nu/kT) - 1} \text{ cal./mol. } ^\circ\text{C.} \quad (8)$$

It would appear from this last equation that for a loose S.H.M. ( $h\nu/kT$  small) this contribution should tend to the value 2 cal./gm. mol.  $^\circ\text{C.}$ , decreasing to zero as  $\nu$  increases. However, we must be careful to apply this formula only in cases where the field is satisfactorily represented by equation (5). This restricts us to cases in which the amplitude of oscillation is small, and the formula breaks down completely as soon as  $h\nu$  becomes of the order  $kT$ , since a fair proportion of the molecules will then be making complete rotations, and the periodic nature of  $V$  has to be taken into account. When there is effectively free rotation we know that the contribution to  $C_v$  approaches  $R/2$  from each degree of freedom. We must be careful, therefore, that we only apply equation (7) when  $h\nu > kT$ . This condition is satisfied in all the cases we have analysed.

All the rotations of types (b) and (c) except one may be taken to be harmonic, *i.e.*, governed by potentials that are essentially parabolic. For the libration II of a water molecule in the field of a negative ion, however, the potential is an unsymmetrical function of the angle of rotation. Fig. 2 shows the complete P.E. function which is seen to exhibit a double minimum; the P.E. hill between them is, however, of height  $20 kT$ , so we need only consider the single minimum problem. The values of  $\theta_0$  (*i.e.*, the angle between the line of centres and the nearer O—H direction) are  $\pm 7.5^\circ$  and  $\pm 19.5^\circ$  for ions of 1 A. and 2 A. respectively; in earlier treatments  $\theta_0$  has been taken as  $0^\circ$  for all cases.<sup>3, 4</sup> We find that near the equilibrium position we may approximate by use of a Morse function, writing

$$V = D' + D(e^{-2a\phi} - 2e^{-a\phi}) \quad (9)$$

where  $D$ ,  $D'$  and  $a$  are constants and  $\phi$  is the angle of rotation away from the equilibrium position. Provided that  $\phi$  never becomes large (as can be shown to be the case in our present calculations for all reasonable temperatures) then the fact that the range of  $\phi$  is not infinite in the Morse curve is not important, and an insignificant error is introduced by assuming that the allowed energy levels are those representing the normal solution of the wave equation in the range 0 to infinity, *i.e.*, that the levels are

$$E_n = D - D' + \frac{a\hbar}{\pi} \sqrt{\frac{D}{2I}} \left( n + \frac{1}{2} \right) - \frac{a^2 \hbar^2}{8\pi^2 I} \left( n + \frac{1}{2} \right)^2 \quad (10)$$

where  $n$  has the values 0, 1, 2 . . . .<sup>8</sup> The contribution to the specific heat can now be written

$$\frac{R}{2} \left\{ \frac{S_3}{f} - \left( \frac{S_2}{f} \right)^2 \right\} \quad (11)$$

where

$$\left. \begin{aligned} f &= \sum_n e^{-E_n/kT} \\ S_2 &= \sum_n E_n e^{-E_n/kT} \\ S_3 &= \sum_n E_n^2 e^{-E_n/kT} \end{aligned} \right\} \quad (12)$$

The values of  $E_n$  increase so rapidly that only a few terms are required in the evaluation of  $f$ ,  $S_2$  and  $S_3$  to obtain sufficiently accurate values for these quantities.

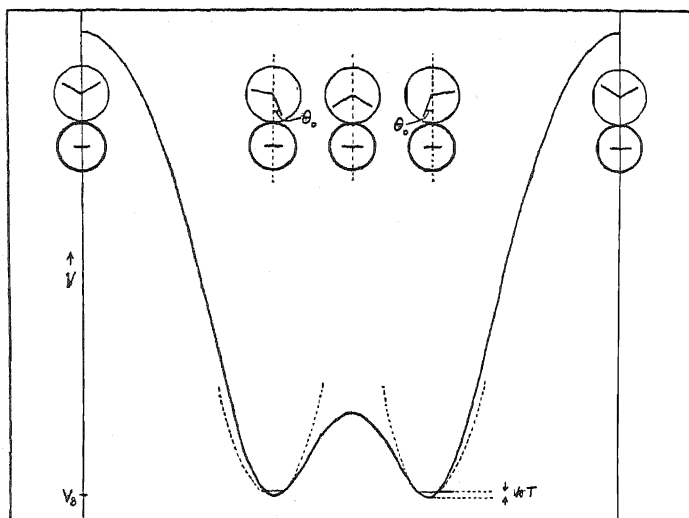


FIG. 2.—P.E. curve for rotation of water molecule in field of cation about axis (c). Dotted curves: P.E. curves for S.H.M.

So far we have not considered the third rotation of the water molecules which we have referred to as axial spin. In this rotation, however, the charge on the central ion does not lead to any variation in the electrostatic energy; the forces controlling this degree of freedom are due to attractions between members of the first and second co-ordination shells. It is quite impossible without a more detailed model both of ordinary pure water and of the structure round a dissolved ion to make any exact calculations of the heat capacity due to this rotation, but there is little reason to suppose that it should differ greatly in the two cases, since neither with water nor with the central ion are the forces of attraction very powerful. In calculating the value of  $\Delta C_p$  we shall accordingly neglect any contribution from this rotation.

We have tacitly assumed in these calculations that the three rotations are independent; this, of course, is not correct, and in a full Hamiltonian and wave equation there are cross terms coupling these rotations to

<sup>8</sup> Morse, *Physic. Rev.*, 1929, **34**, 57.

each other. However, we have chosen the system of normal coordinates, and provided that the amplitude of the librations is not large, these cross terms will be small (of third order) and their effect upon the calculated energies and heat capacities of no great importance in this work where we are concerned primarily with orders of magnitude.

#### 4. Rotational Degrees of Freedom in Pure Water.

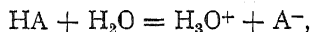
Experimentally the problem of molecular rotation in liquid water has been studied spectroscopically. Infra-red and Raman spectra studies of water have been the subject of much controversy,<sup>9</sup> especially in regard to the low frequency bands which are attributed to hindered molecular rotation and translation. It seems very probable, however, that a rather faint, ill-defined band at about  $500\text{ cm.}^{-1}$  ( $1.5 \times 10^{13}\text{ sec.}^{-1}$ ) does exist corresponding to restricted rotation of the water molecules, together with a sharper band at about  $200\text{ cm.}^{-1}$  arising from "hindered translation."<sup>10</sup> It appears then that the motion of at least some of the molecules in liquid water is in some way restricted, but the exact interpretation is still rather uncertain. There is no reliable method at present of estimating what proportion of water molecules are affected by these restrictions, nor of deciding which of the rotational degrees of freedom are involved. The large difference between the heat capacities of ice and water probably indicates moreover that, although water has a quasi-crystalline structure in which the water molecules are oriented, the binding forces are not sufficiently powerful to reduce substantially the contribution of the rotational degrees of freedom to the heat capacity. On the other hand, however, we must bear in mind that if the rotations are completely unrestricted, then the contribution to  $C_p$  from each rotation is only  $\frac{1}{2}R$ , i.e.  $1\text{ cal./g. mol. }^\circ\text{C.}$  We shall, however, assume for the present that in pure water the rotations which we have considered contribute  $2\text{ cal./g. mol. }^\circ\text{C.}$  to the heat capacity of the system. If this is not so, but an appreciable proportion of the molecules have their rotations either frozen out or effectively unrestricted, then the values of  $\Delta C_p$  evaluated below will have to be reduced accordingly.

#### 5. Results of Calculations.

The results of our calculations applied to ions of 1 Å. and 2 Å. radius, and at  $0^\circ$ ,  $25^\circ$ , and  $50^\circ\text{ C.}$  are summarised in Table I. As previously mentioned we have assumed  $C_v$  and  $C_p$  to be equal for the present purpose.

#### 6. Heat Capacity Changes Accompanying Ionisation.

We are now in a position to calculate the heat capacity change accompanying the ionisation:



in so far as this is due to librational effects and to the simple electrostatic term.

<sup>9</sup> E.g., Hibben, *J. Chem. Physics*, 1937, **5**, 166, 994; Rao and Koteswaram, *ibid.*, 1937, **5**, 667.

<sup>10</sup> (a) Cross, Burham and Leighton, *J. Am. Chem. Soc.*, 1937, **59**, 1134; (b) Cartwright, *Nature*, 1935, **135**, 872; **136**, 181.

The contribution to  $\Delta C_p$  from orientational effects,  $(\Delta C_p)_{or.}$ , is equal to the difference between the heat capacity of the rotational degrees of freedom in pure water and of water molecules oriented by the two ions formed. To obtain a rough estimate of  $\Delta C_p$  we assume that, in pure water, each rotational degree of freedom contributes 2 cal./°C. to the heat capacity of the system. By subtracting our calculated heat capacities from 2, we obtain the heat capacity change corresponding to the partial freezing out of this degree of freedom. Assuming both the hydroxonium ion and the anion formed on ionisation to be four-co-ordinated we have evaluated the contributions to  $\Delta C_p$  from orientational effects. These are summarised in Table II. Outside the first tetrahedral shell we have regarded Born's equation as being valid, and table II contains the values of the contributions,  $(\Delta C_p)_{B.C.}$ , from the simple charging process. This contribution arises from the change of the charge energy with temperature due to the temperature dependence of the dielectric constant, and has been calculated using Wyman and

TABLE I.

*Orientation by negative ion—*

				$C_p$			
Libration I	$r$	$K \times 10^{12}$	$\nu \times 10^{-13}$	0°	25°	50° C.	
	1 A.	6.54	3.30	0.20	0.28	0.36	
	2 A.	1.34	1.41	1.23	1.29	1.41	
Libration II	$r$	$a$	$D \times 10^{12}$	$D' \times 10^{12}$	0°	25°	50° C.
	1 A.	0.925	3.285	8.244	0.23	0.32	0.40
	2 A.	1.104	4.037	7.095	1.39	1.48	1.57

*Orientation by positive ion—*

				$C_2$		
Libration I	$r$	$K \times 10^{12}$	$\nu \times 10^{-13}$	0°	25°	50° C.
	1 A.	0.80	1.74	0.97	1.08	1.18
	2 A.	0.58	1.48	1.18	1.28	1.36
Libration II	$r$	$a$	$D \times 10^{12}$	$D' \times 10^{12}$	$C_p$	
	1 A.	2.06	1.39	1.23	1.33	1.42
	2 A.	0.58	0.74	1.74	1.78	1.85

Ingalls' most recent data<sup>11</sup> for the dielectric constant of water, and taking the effective radius of the ion as that of the four-co-ordinated structure.

Estimates of the total contribution to  $\Delta C_p$  from these two effects are collected at the foot of the table for ionisations yielding ions of various sizes.

It is interesting to note that while  $(\Delta C_p)_{or.}$  decreases with rising temperature,  $(\Delta C_p)_{B.C.}$  increases. These two effects cancel almost exactly, so that the total contribution to  $\Delta C_p$  from these sources remains practically independent of temperature. This cancelling of temperature coefficients may well account for the temperature independence of  $\Delta C_p$  which seems to characterise acid-base equilibria. We also note that although the magnitude of  $\Delta C_p$  may be explained by simple electrostatic effects, provided we assume an ionic radius sufficiently small, the temperature independence of  $\Delta C_p$  cannot be accounted for by this alone.

The experimentally observed values of  $\Delta C_p$  for ionisations of the type under consideration are usually about -40 cal./°C. Our values

<sup>11</sup> Wyman and Ingalls, *J. Am. Chem. Soc.*, 1938, **60**, 1182.

calculated on the basis of a simple model are considerably lower than this figure, and we now examine possible discrepancies in our treatment.

As mentioned above, the work of Stewart<sup>7</sup> indicates that the co-ordination number of water in ionic solutions is nearly five while we

TABLE II.

- ( $\Delta C_p$ ) <sub>or.</sub> Contributions per molecule oriented.				0°	25°	50° C.
<b>Negative Ions.</b>						
1 A. Libration I	.	.	.	1.80	1.72	1.64
" II	.	.	.	1.77	1.68	1.60
				<u>3.57</u>	<u>3.40</u>	<u>3.24</u>
2 A. Libration I	.	.	.	0.77	0.71	0.59
" II	.	.	.	0.61	0.52	0.43
				<u>1.38</u>	<u>1.23</u>	<u>1.02</u>
<b>Positive Ions.</b>						
1 A. Libration I	.	.	.	1.03	0.92	0.82
" II	.	.	.	0.77	0.67	0.58
				<u>1.80</u>	<u>1.59</u>	<u>1.40</u>
2 A. Libration I	.	.	.	0.82	0.72	0.64
" II	.	.	.	0.26	0.22	0.15
				<u>1.08</u>	<u>0.94</u>	<u>0.79</u>
- ( $\Delta C_p$ ) <sub>B.C.</sub> Contributions per Ion formed.						
1 A. . . . .	.	.	.	2.85	3.40	4.30
2 A. . . . .	.	.	.	2.20	2.60	3.35
- {( $\Delta C_p$ ) <sub>or.</sub> + ( $\Delta C_p$ ) <sub>B.C.</sub> } for formation * of:—						
Positive ion 1 A.	.	- ( $\Delta C_p$ ) <sub>or.</sub>		21.5	20.0	18.6
Negative ion 1 A.	.	- ( $\Delta C_p$ ) <sub>B.C.</sub>		5.7	6.8	8.6
				<u>27.2</u>	<u>26.8</u>	<u>27.2</u>
Positive ion 1 A.	.	- ( $\Delta C_p$ ) <sub>or.</sub>		12.7	11.2	9.7
Negative ion 2 A.	.	- ( $\Delta C_p$ ) <sub>B.C.</sub>		5.0	6.0	7.7
				<u>17.7</u>	<u>17.2</u>	<u>17.4</u>
Positive ion 2 A.	.	- ( $\Delta C_p$ ) <sub>or.</sub>		9.8	8.7	7.2
Negative ion 2 A.	.	- ( $\Delta C_p$ ) <sub>B.C.</sub>		4.4	5.2	6.7
				<u>14.2</u>	<u>13.9</u>	<u>13.9</u>

\* All ions assumed 4-coordinated.

have assumed the value four. If we take five as the more correct value, then the calculated values of ( $\Delta C_p$ )<sub>or.</sub> must be increased by one-quarter. We cannot even so account for  $\Delta C_p$ 's of more than - 32 cal./°C. at 25° C. unless we consider ions of less than 1 A. radius. We do

not propose to discuss at length the effective radii of ions. This has been done by Baughan<sup>12</sup> who concludes that a radius of 1 Å. is not unreasonably small. We regard this as a lower limit, however, so we shall not consider the possibility of smaller ionic radii as an explanation of the low values of  $\Delta C_p$  we have obtained.

So far we have only considered restrictions of the rotational degrees of freedom of the water molecules. We now consider briefly other possible restrictions on their motion.

Current theories of liquid structure assign to each molecule a "free volume,"  $v_f$ , which depends on the temperature. The free volume arises from the translational motion of the molecules because their mobility depends on the forces between them and on their mutual orientations. Its exact interpretation is complicated but, roughly, it represents the volume or cell in which each molecule is free to move, and inside which it is confined for a considerable number of vibrations by collisions with its neighbours. We cannot yet evaluate the free volume for water with any certainty since it depends on the packing of the water molecules; but we can, however, make qualitative predictions as to the influence of ions on its value.

Morgan and Warren have concluded from their X-ray analysis of water at 1.5° C., that a subsidiary shell of water molecules (containing 2-3 molecules) exists between the first and second pure tetrahedral coordination shells (as found, *e.g.*, in ice). The explanation is that some water molecules are able to move into the vacant spaces to be found in the comparatively open tetrahedral structure. Stewart's work indicates that more of the interstitial spaces are filled round an ion than in pure water; consequently there will be a reduction in the free volume of the oriented molecules.

Now the free volume enters directly as a factor in the partition function of a liquid so that the contribution of the free volume to the heat capacity depends on the way in which  $v_f$  varies with temperature.

Stearn and Eyring<sup>13</sup> have expressed the free volume of pure water in the form of a purely empirical equation

$$v_f = bT^n \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where  $b$  is constant, and to account for the heat capacity of water,  $n$  is taken to be 5. Now if we can regard  $b$  as remaining constant, then a decrease in the free volume of the water molecules near an ion will mean a decrease in  $n$ , this in turn resulting in a decrease in the contribution to the heat capacity from the free volume. There are, however, no theoretical grounds for supposing that  $b$  has the same value in pure water and ionic solutions, so that this argument is inconclusive.

The calculation of the contribution to  $\Delta C_p$  arising from the change in free volume is difficult, but it may be found possible to approach the problem by considering the free volume in terms of

(a) the two-dimensional movement of the water molecules at a constant distance from the ion (lateral translation), and

(b) the allowed displacements outward from the ion (radial translation);

(a) may be described by allocating to each molecule a "free area" on the surface of the sphere on which it moves and (b) by allocating to each molecule a "free length." Eley and Evans have derived an

<sup>12</sup> Baughan, *J. Chem. Physics*, 1939, 7, 951.

<sup>13</sup> Stearn and Eyring, *ibid.*, 1937, 5, 113.

expression for the free area but as yet the treatment is not precise enough to determine its temperature dependence, so the change in heat capacity due to this factor is not known. The radial vibration of the water molecules against the ion may be analysed roughly in terms of an S.H.M. We find that no appreciable decrease in  $\Delta C_p$  is likely to arise from this motion.

Finally we have to consider the difference between the free volume of the liquid for the undissociated acid molecule HA, and the co-ordinated anion  $A^-$ . Again we have no means of evaluating the difference between the temperature dependence of the free volume in the two cases.

We now see that the value of  $\Delta C_p$  may be determined by additional subsidiary factors besides those we have considered in detail, so that the somewhat low values we have obtained are not unexpected. In this connection we notice that in the calculation of the entropy of solution of ions,<sup>4</sup> the contributions to the final values of  $\Delta S$  from the libration and Born charging effects vary from about  $\frac{1}{4}$  to  $\frac{2}{3}$  of the total  $\Delta S$ .

Consequently we regard our calculations as satisfactory justification of the qualitative picture of solvent molecule orientation previously employed to account for the heat capacity changes accompanying ionisation. We would, however, emphasise that an interpretation of such heat capacity changes solely on the basis of the charge type of the reaction cannot be complete since isoelectric reactions, for which we might expect  $\Delta C_p$  to be zero, are known which have large positive values of  $\Delta C_p$  (e.g., the dissociation of the trimethylammonium ion).<sup>5</sup> This indicates that more specific solute-solvent interaction of a quasi-chemical nature may also be of importance in determining  $\Delta C_p$ .

## 7. Summary.

The possibility of applying statistical mechanics to the calculation of ionic heat capacities has been investigated and applied to the problem of the change in heat capacity accompanying the ionisation of acids. It is shown that by considering the influence of the ions on the freedom of rotation of water molecules in their neighbourhood, we may account for most of the observed change. The values obtained are discussed and possible additional effects which may be of importance are considered. At present further advance in this field is mainly limited by our rather meagre knowledge of the nature of liquid water.

The authors wish to express their thanks to Prof. W. F. K. Wynne-Jones for valuable criticism and advice particularly in the early stages of this work. One of us (D. H. E.) is indebted to the Trustees of the Ramsay Memorial Fund for a Fellowship.

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# PERMEABILITY OF ORGANIC POLYMERS.

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It has been demonstrated<sup>1</sup> that diffusion of permanent gases in organic polymers obeys Fick's law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

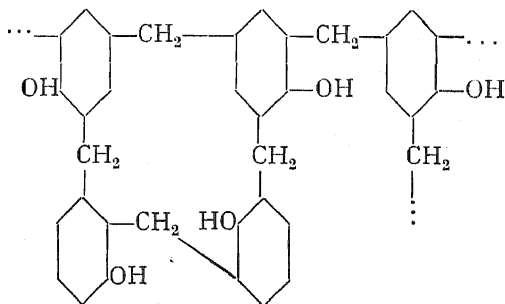
and that  $D = D_0 e^{-\frac{E}{RT}}$  where  $E$  is a characteristic energy of activation, and  $D_0$  a temperature independent factor. Similarly the permeability constant  $P$ , defined by

$$P = -D \frac{\partial c}{\partial x}$$

(for a standard concentration gradient) obeyed the law  $P = P_0 e^{-\frac{E_1}{RT}}$ . In terms of these findings a picture of the diffusion process was given<sup>2, 3</sup> and relations were defined between diffusion in rubber-like polymers, ionic crystals, metals, and liquids.<sup>3</sup>

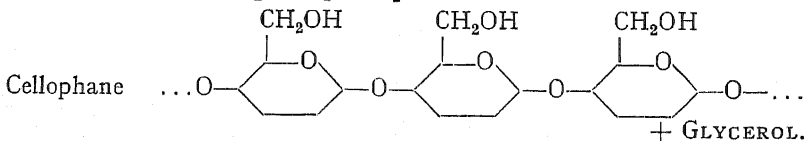
As for rubber-like polymers, so for more rigid membranes,<sup>4</sup> the permeability follows the expression  $P = P_0 e^{-\frac{E_1}{RT}}$ . The extension of results from elastic to rigid membranes promised data of importance in the theory of these non-specific types of activated diffusion. Measurements were therefore undertaken using the materials

Bakelite



Ebonite  $(C_5H_8S)_n$ .

Polyethylene  $\dots -CH_2-CH_2-CH_2-\dots$



<sup>1</sup> H. Daynes, *Proc. Roy. Soc., A*, 1920, **97**, 286.

<sup>2</sup> R. M. Barrer, *Trans. Faraday Soc.*, 1939, **35**, 628.

<sup>3</sup> *Ibid.*, 644.

<sup>4</sup> J. de Boer and J. D. Fast, *Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 317.

Bakelite is an irregular three-dimensional network, normally of a micellar structure. It may be regarded as an hydroxyl-containing membrane different from the fibrillar micelle of cellulose derivatives studied earlier,<sup>4</sup> and here exemplified by cellophane. Ebonite represents the final product of vulcanisation of rubber. In its high sulphur content it resembles the polysulphide rubbers, which are extremely impermeable to gases,<sup>1</sup> but the parent substance is polyisoprene, a rubber through which gases diffuse easily. Polyethylene in appearance is wax-like, but some of its properties suggest those of rubbers. It has a special interest because it represents a transition between a wax which would be expected to be impermeable, and a hydrocarbon rubber, which is permeable to gases.

Polyethylene membranes were prepared by moulding at  $< 80^{\circ}$  C. in a metal press.<sup>2</sup> High temperatures were avoided since the membrane then tended to become full of bubbles. Bakelite, ebonite and cellophane discs were cut from sheets of the commercial product.

TABLE I.—PERMEABILITY OF ORGANIC MEMBRANES.

Sheets of the commercial product.	System.	Temperature.	Permeability Constant $P \times 10^6$ (c.c./sec./cm <sup>2</sup> /mm./cm. Hg press.).
<b>The Permeability Constants.</b>  In Table I are given the permeability data for the membranes employed. While studying ebonite it was observed that under vacuum and at temperatures only slightly above room temperatures the membrane itself was evolving gas at a constant very slow speed. The rate of this decomposition was comparable to the rate of permeation of	H <sub>2</sub> -Bakelite .	75.5	0.00052
		57.0	0.00035
		45.0	0.00026
		34.2	0.000164
		20.0	0.000095
	N <sub>2</sub> -Bakelite .	75.0	0.00027
		56.6	0.000115
		47.2	0.000083
		37.5	0.000048
		36.1	0.000047
	He-Ebonite .	20.0	0.0000095
		18.0	0.0000085
		82.5	0.0072
		67.0	0.0047
		54.5	0.00305
	H <sub>2</sub> -Ebonite .	43.7	0.00255
		17	0.00105
		83.0	0.00192
		67.0	0.00141
		49.0	0.00091
N <sub>2</sub> -Ebonite .	34.0	0.00045	
	67.2	≤ 0.000025	
	He-Polyethylene	17.0	0.0067
		22.6	0.0082
		30.8	0.0115
38.5		0.0184	
H <sub>2</sub> -Polyethylene		22.6	0.0110
	34.8	0.019	
	37.2	0.021	
	56.0	0.053	
	85.0	0.063	
He-Cellophane .	74.0	0.044	
	52.0	0.0148	

hydrogen and helium through it, but faster than the permeation velocity of nitrogen. The permeation velocities of these gases had therefore to be found by difference, and the figure given for nitrogen (Table I) is an upper limit only.

### The Influence of Temperature.

In Fig. 1 are given the curves  $\log P$  against  $1/T$  ( $T = ^\circ\text{K}.$ ) for bakelite, ebonite, cellophane and polyethylene membrane-gas diffusion

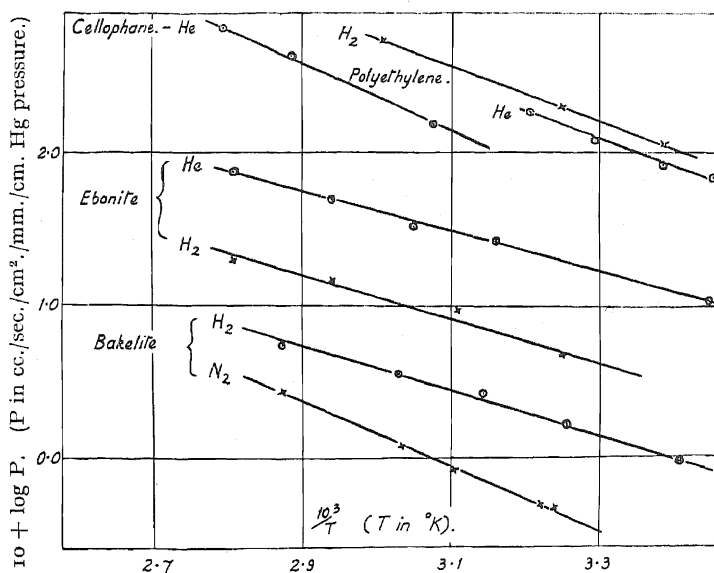


FIG. 1.

systems. In Table II are collected the temperature coefficients of the permeation processes expressed as cal./mol. of diffused gas. In addition Table II gives the coefficients for some hydrogen-cellulose derivative diffusion systems studied by De Boer and Fast.<sup>4</sup> It is surprising that

TABLE II.—TEMPERATURE COEFFICIENTS OF PERMEABILITY CONSTANTS OF GAS MEMBRANE DIFFUSION SYSTEMS.

System.	Temperature Coefficient (Cal./Mol.).
H <sub>2</sub> -Bakelite . . . .	5100
H <sub>2</sub> -Ebonite . . . .	6500
H <sub>2</sub> -Polyethylene . . . .	8050
H <sub>2</sub> -“Triacel” . . . .	7500
H <sub>2</sub> -Celluloid . . . .	5650
H <sub>2</sub> -Regenerated Cellulose . . . .	7600
H <sub>2</sub> -Nitrocellulose . . . .	5700
He-Ebonite . . . .	5900
He-Polyethylene . . . .	7700
He-Cellophane . . . .	9900
N <sub>2</sub> -Bakelite . . . .	10500

these temperature coefficients are so small, since the membranes are rigid rather than rubber-like. The temperature coefficient of the permeability of the N<sub>2</sub>-bakelite system is, however, twice as large as the corresponding coefficient for H<sub>2</sub>-bakelite. With increasing internal rigidity the required energy of activation becomes more sensitive to the molecular dimensions of the diffusing substance.

The permeability constant and temperature coefficient of permeability of gas-polyethylene systems prove to be very close to those for gas-rubber systems<sup>2</sup> and to be similar for hydrogen and helium. In this property polyethylene resembles a rubber rather than a rigid

membrane, so that the mechanism of permeation is likely to resemble that for diffusion in rubbers.<sup>2, 3</sup>

### Relative Permeation Velocities.

The permeation velocity of hydrogen through rubbers<sup>1</sup> is 10-fold greater than through most of the cellulose derivatives of De Boer and Fast. Regenerated cellulose is only 1/100-fold as permeable as rubber. The hydrogen permeabilities of celluloid,<sup>4</sup> chloroprene,<sup>2</sup> ebonite and bakelite at room temperature stand in the approximate ratio

$$1.6 : 2 : 0.2 : 0.10$$

while the temperature coefficients (save for chloroprene, 8300 cal./mol.) are similar. The temperature coefficients include the coefficients of the solubility, and the ratio of permeabilities depends *inter alia* on the ratio of solubilities. It also depends on whether the diffusion occurs within micelles, or only in intramolecular spaces. That diffusion is of the grain-boundary type might be argued from the much smaller permeability through the rigid membranes,\* coupled with a *smaller* temperature coefficient (related to the activation energy for diffusion).

The ratio of permeation velocities through bakelite and ebonite are

$$\begin{array}{ll} \text{Bakelite} & \quad \quad \quad \text{H}_2 : \text{N}_2 = 1.0 : 0.1, \text{ at room temperature.} \\ \text{Ebonite} & \quad \quad \quad \text{He} : \text{H}_2 : \text{N}_2 = 1.0 : 0.3 : 0.005, \text{ at } 67^\circ \text{ C.} \end{array}$$

The strong specificity of these ratios is characteristic of activated diffusion through rigid membranes,<sup>1, 5</sup> and is sufficient to suggest that ebonite or bakelite would be good fractionating membranes for separating mixtures of simple gases. The permeability is greater than that of silica glass,<sup>5</sup> which has been used for fractionation,<sup>6</sup> but is too low for a rapid separation. There would, however, be at least a 200-fold fractionation between nitrogen and helium, using an ebonite diffusion membrane.

The effect of vulcanisation of rubber upon its permeability has often been discussed. Several per cent. of combined rubber has no effect.<sup>2, 5</sup> According to the theory advanced earlier, however,<sup>2, 3</sup> if sufficient sulphur were combined with the rubber, cross-linking of chains would produce a rigid network, whose permeability for larger molecules would be negligible. Ebonite represents such a membrane, and it is seen that this netted structure is sufficiently open for helium to diffuse about as easily as through rubber. Hydrogen, however, cannot diffuse so readily and nitrogen can scarcely diffuse at all. Thus the influence of the combined sulphur content upon permeability depends upon the diameter of the diffusing molecule, as well as the amount of sulphur.

### Summary.

Data are given for the permeability of membranes of bakelite, ebonite, polyethylene, and cellophane to the gases helium, hydrogen and nitrogen, over the range 17 to 85° C. From the temperature coefficients, values of

$E_1$  are obtained for the expression  $P = P_0 e^{-\frac{E_1}{RT}}$  ( $P$  denotes the permeability constant).

\* Diffusion down grain boundaries requires a smaller activation energy than diffusion within the micelle.

<sup>4</sup> R. M. Barrer, *J. Chem. Soc.*, 1934, 378.

<sup>6</sup> W. Watson, *ibid.*, 1910, 97, 810.

The results are discussed in terms of the theory of non-specific activated diffusion through rigid membranes, and are related to previous data on rubber-like and cellulosic membranes.

The experimental work was carried out in the Laboratory of Colloid Science, during the tenure of a Research Fellowship at Clare College, Cambridge.

*The Chemical Laboratories,  
The Technical College,  
Bradford.*

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### REVIEWS OF BOOKS.

**The Nature of the Chemical Bond and the Structure of Molecules and Crystals.** By LINUS PAULING (Cornell University Press, Ithaca, New York, 1939. London: Humphrey Milford, Oxford University Press). Pp. xiv + 429. Pre-war price 21s.; present quotation 28s.

The author of this book is now so well known in this country, through his papers and his apostles, that any elaborate statement of his qualifications to write such a book as this is quite unnecessary. It is sufficient to say that Pauling has a sound grasp of mathematical physics, a deep interest in chemistry, great ingenuity, and no inhibitions; and that this rare and happy combination of qualities has enabled him to play a very important and lively part in the recent application of wave-mechanics to the solution of chemical problems. All who have researched in the field of molecular structure have long awaited this book.

The first applications of the new mechanics to chemistry were comparatively exact treatments of simple but fundamental problems and made difficult reading for the chemist. As more complex problems were tackled the treatments became more approximate and came to depend increasingly upon the use of conceptions which had been obtained by generalising from the particular cases that lent themselves to precise treatment. In the present work, the main physical conclusions are presented as a set of postulates from which the reader is invited to start; and from there on little is asked of him save the ability to do simple arithmetic. The author shows how they suggest new ways of analysing a great number and variety of old and new data, and how, as a result, fresh conclusions can be drawn which are extremely illuminating and are directly useful to the chemist. While most of the book is concerned with the structure of individual molecules and with problems centring around relatively normal covalent bonds, the hydrogen bond gets a delightful chapter to itself, and the structure of the crystalline state is succinctly but excellently discussed in two; so most of the important topics are covered adequately.

The author has aimed at presenting the subject as he sees it; and when, as often happens in this far-from-finished story, other workers hold views different from his, he naturally stresses his own. But the other views are usually mentioned, and the sceptical reader can find out most

of what he should read in order to obtain a more complete picture. On purely scientific grounds the book may be criticised for over-simplifying the story and for giving it a premature happy ending. Much of the simplification is deliberate and is entirely justified by the need for clarity in this comparatively elementary book; but some is due to a tendency to take things for granted. So, for example, the author assumes without proof that the electric dipole moment of a purely covalent link is small or is zero. It may be—or it may not. The impression of certainty comes partly from this simplification and partly from tricks of style. By drawing comparatively detailed deductions from his working hypotheses the author leads us to think that he has great faith in them; which probably is not altogether true. These characteristics undoubtedly make the book more readable; but the general reader, who may be slightly intoxicated by them, is advised to take a grain or two of salt as he reads.

The compromise between accuracy and readability, necessary throughout such a book as this, must be especially difficult to make satisfactorily in the introductory sections. Little is known with certainty of the characteristics of the "average chemist", but if it may be assumed that this permeability is not greater than that of a third year honours student of good second-class ability, then we can say definitely that the introductory sections should be fuller. By presenting a series of postulates and arguing from them the author follows a correct but slightly bleak procedure. A brief exposition of the part played by the wave-equation in chemical problems, of the physical significance of a wave-function, and of the way in which this leads to the possibility of a hybrid wave-function giving increased (or decreased) stability in the system, would help to relate the postulates made to the conceptions which the reader is likely to have.

This book is the most complete attempt so far made to explain chemical and physical properties consistently on a small number of working hypotheses derived from wave-mechanics. Successful as it is, it marks only the beginning of the process of consolidation of recent advances which is now necessary. As is only to be expected, the need for further cross-referencing of facts and arguments, as well as the filling of gaps, is sometimes evident. Thus, in the discussion of heats of formation of bonds, the emphasis is upon resonance between covalent and ionic structures: later, in that on bond lengths, the possibility of resonance of single with multiple bonds is introduced; but there is no consideration of the possible repercussion of this upon the previous argument. This instance emphasises the need for unifying the discussion of properties still further when trying to draw conclusions about structure.

Although this book has imperfections, it is, on balance, the most valuable work on molecular structure in relation to chemistry which has appeared for a number of years. Certainly it will for some time hence be the foundation for further discussions of the subject. Owing to the war it is now quite expensive and difficult to obtain; but all who can will be well-advised to buy it, read it, and re-read it.

L. E. S.

**Terrestrial Magnetism and Electricity.** Edited by J. A. FLEMING.  
(London: McGraw-Hill Publishing Co. Ltd., 1939. Pp. xii + 794.  
Price 52s. 6d.)

This encyclopædic volume appears as the eighth number of a series of monographs on the physics of the earth, published under the direction of various committees of the National Research Council. It represents the result of a piece of well-co-ordinated team-work, and its twelve main chapters deal with The Earth's Magnetism and Magnetic Surveys, Magnetic Instruments, Magnetic Prospecting, Atmospheric Electricity and Instruments used therein, Earth-currents, Causes of the Earth's Magnetism, Some Problems of Terrestrial Magnetism, Radio-exploration of the Outer Atmosphere, The Upper Atmosphere, The Aurora Polaris, and Thunder-and Shower-Clouds.

It would be unprofitable to attempt to go into detail in a short review of a work—itsself only part of a larger scheme—conceived on so great a scale. It is sufficient to say that the book provides a vast fund of information for the specialist, that it is thoroughly physical in its outlook, and may be read with pleasure by any physicist interested in the problems of terrestrial magnetism.

The authors—each an authority in his particular branch of the subject—have provided a comprehensive bibliography which covers more than fifteen hundred separate entries.

It goes without saying that the book is admirably produced. No comprehensive science library can afford to be without it.

A. F.

**Static and Dynamic Electricity.** By Prof. W. R. SMYTHE. (London: McGraw-Hill Publishing Co. Ltd., 1939. Pp. xviii + 560. Price 40s.)

Professor Smythe is exercised concerning the troubles of the average graduate student who, though he may tackle readily enough the orthodox bookwork problems of advanced electrical theory, is apt to be floored by the problems which he meets in research and technical work—problems “which fall outside the routine types, and so must be worked out from first principles.” For twelve years past he has given a course to advanced students training in various branches of applied physics, and the present book is the result.

It must be adjudged to be successful, and the student who has worked carefully through the book should not suffer from lack of flexibility in handling those tools which should form an important part of the stock of a worker in the field of applied electrical theory.

Two- and three-dimensional potential problems, magnetic interactions of currents and electromagnetic induction, transient phenomena in networks, alternating and eddy currents, electromagnetic waves and special relativity—these are examples of the topics discussed in a book which is at once thoroughly practical and scholarly.

It is a book which deals with selected topics, “based directly on the macroscopic experimental facts,” and the student of honours grade who is likely to specialise in applied physics will derive great benefit from its study.

A. F.

AUG. 1940

LIBRARY

## MOLECULAR INTERACTIONS AT OIL/WATER INTERFACES.

### PART I. MOLECULAR COMPLEX FORMATION AND THE STABILITY OF OIL IN WATER EMULSIONS.

BY J. H. SCHULMAN AND E. G. COCKBAIN.

*Received 15th February, 1940.*

It has been shown recently<sup>1</sup> that when certain substances are injected under monolayers of cholesterol, glaidin, etc., spread on the surface of water, molecular association occurs. Two distinct phenomena could be observed. If interaction occurred only between the polar groups of the monolayer substance and the injected compound, adsorption of the latter on the monolayer took place with concomitant changes in the surface potential, and in some cases, the rigidity of the film. When, in addition to the polar interaction, there was strong association between the non-polar parts of the two reacting species, a penetration of the monolayer occurred with changes in the surface pressure as well as the surface potential. The non-polar association was very sensitive to the stereochemical configurations of the two reacting molecules, since a suitable stereochemical relationship permits the close adlineation of the molecules in the interface. In regard to various polar groups, the hydroxy group of cholesterol and the amino groups of proteins were found to be particularly reactive.

Such results on the formation of inter-molecular complexes are of importance in connection with the formation and stability of oil in water, or water in oil emulsions, since the phenomenon of penetration permits of extremely low interfacial tension, much below that which either component can produce separately. From a study of the properties of these emulsions it was seen that reactions taking place at the oil-water interface were closely analogous to the corresponding reactions at an air-water interface, which have been investigated by the method of surface films.

#### Experimental.

Systems composed of mineral oil "nujol" and water were studied in the presence of various emulsifying agents. In some cases emulsification occurred spontaneously. If, for example, an aqueous solution of sodium cetyl sulphate is poured into a solution of cholesterol in "nujol," extensive emulsification occurs without any further shaking, although shaking by hand for a few seconds improves the emulsification. In other cases an emulsifying machine was necessary to produce emulsification.

<sup>1</sup> Schulman and Rideal, *Proc. Roy. Soc. B*, 1937, **122**, 29, 46.



The stability of the emulsions was measured by observing the time required for the first visible signs of separation of the two phases. Such a criterion for emulsion stability is dependent on the efficiency of the emulsification process and on the degree of separation which one recognises as clearly visible. However, it is a satisfactory method of comparing the relative stability of different emulsions prepared under the same circumstances.

### Influence of Non-Polar Steric Factors on Complex Formation of Emulsion Stability.

Schulman and Stenhagen<sup>2</sup> showed that strong complexes were formed at a water/air interface between sodium cetyl sulphate and cholesterol, cetyl alcohol or elaidyl alcohol ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}$  trans isomer). On the other hand, sodium cetyl sulphate formed only a weak complex with oleyl alcohol which is the *cis* isomer corresponding to elaidyl alcohol. In the case of oleyl alcohol, the *cis* configuration of the hydrocarbon chain prevented close adlineation between the sodium cetyl sulphate and the oleyl alcohol molecules at the interface, with the result that the van der Waals forces of adhesion were small and the molecular complex correspondingly weak. To establish whether the same stereochemical factors affected the stability of complexes at an oil/water interface, emulsions of "nujol" in water were prepared, emulsification being brought about by hand-shaking for ten seconds. In the "nujol" was dissolved the oil soluble agent (cholesterol, cetyl alcohol, etc.) and in the water, the sodium cetyl sulphate. Concentrations employed are given in Table I.

TABLE I.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
140 mg. cholesterol	—	No emulsion.
140 mg. cholesterol	75 mg. Na cetyl sulphate	Very poor emulsion.
	75 mg. Na cetyl sulphate	Excellent emulsion. (liquid)
140 mg. oleyl alcohol	75 mg. Na cetyl sulphate	Very poor emulsion.
140 mg. elaidyl alcohol	75 mg. Na cetyl sulphate	Very good emulsion (viscous)
140 mg. cetyl alcohol	75 mg. Na cetyl sulphate	Very good emulsion. (grease)

It is to be noted that the state of the interfacial film as observed at the air-water interface, *i.e.* solid, viscous or liquid, is reflected in the nature of the resultant emulsion being respectively a grease, viscous or a liquid emulsion. Thus a cholesterol film penetrated by cetyl sulphate is a liquid film giving a very fluid emulsion when these two stabilising agents are used. But a cetyl alcohol film goes solid on penetration by cetyl sulphate, these two stabilising agents produce a grease for the emulsion.

The viscosity of the penetrated elaidyl alcohol film lies between these two extremes, likewise does the viscosity of the resultant emulsion.

This phenomenon can be easily understood if one imagines that the oil droplets which have a solid interfacial film round them behave as

<sup>2</sup> Schulman and Stenhagen, *Proc. Roy. Soc. B*, 1938, **126**, 356.

solid spheres, which cannot slip past one another by distortion, as with the liquid spheres, thus giving a great rigidity to the emulsion.

In spite of the qualitative nature of the above experiments, it can be concluded that stabilisation of the oil in water emulsions has been effected by a complex formation at the oil/water interface between the oil-soluble and the water-soluble components added. Furthermore, it is apparent that the stability of a complex at the oil/water interface is very sensitive to non-polar stereochemical relationships, just as it is at a water/air interface. The weak emulsifying power of cetyl sulphate plus elaidyl alcohol (*trans* isomer) illustrates the point particularly clearly. Table I shows the effect of the stereochemical configuration of the oil-soluble component on molecular complex stability and on emulsion stability. The stereochemical configuration of the water-soluble component is likewise important: "Nujol" in water emulsions were prepared using cetyl alcohol or cholesterol as the oil soluble component and sodium stearate, sodium oleate or sodium elaidate as the water soluble component of the emulsifying agent.

Concentrations used are given in Table II, emulsification being brought about as before by hand-shaking.

TABLE II.

10 c.c. "Nujol."	40 c.c. H <sub>2</sub> O.	Remarks.
140 mg. cetyl alcohol	250 mg. sodium stearate	Stability of the emulsion good. Viscosity high, giving the emulsion grease-like properties.
140 mg. cetyl alcohol	250 mg. sodium elaidate	Stability good.
140 mg. cetyl alcohol	250 mg. sodium oleate	Stability poor.
140 mg. cholesterol	250 mg. sodium oleate	Stability very poor.
140 mg. cholesterol	250 mg. sodium elaidate	Stability good.

The results in Table II show that sodium elaidate, which is the *trans* isomer corresponding to sodium oleate, forms much stronger complexes with cetyl alcohol or cholesterol than does sodium oleate. This complex formation is difficult to determine quantitatively at an air/water interface owing to the strong and rapid capillary action of the oleate and elaidate.

### Effect of Polar Interaction on Complex Formation and Emulsion Stability.

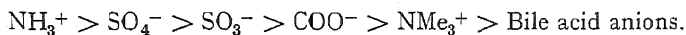
Schulman and Rideal<sup>1</sup> have shown that the penetration of a monolayer at an air/water interface by substances in the underlying solution and the stability of the resulting mixed film are strongly dependent on the degree of interaction between the polar groups of the film substance and the penetrating compound. For example, sodium cetyl sulphate rapidly penetrates a film of cholesterol and a stable equimolecular complex is formed. By substituting cholesterol acetate or cholesterol stearate for the cholesterol only a negligible interaction occurs. It is shown below that the stability of molecular complexes at an oil/water interface is likewise strongly dependent on the degree of polar interaction between the two components of the complex. Thus, Table III shows that a mixture of cetyl sulphate and cholesterol stearate (or cholesterol acetate)

does not stabilise "nujol" in water emulsions whereas that of cetyl sulphate and cholesterol gives stable emulsions. Emulsification was produced by hand-shaking.

TABLE III.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
140 mg. cholesterol stearate	250 mg. cetyl sulphate	No emulsion.
140 mg. cholesterol acetate	250 mg. cetyl sulphate	Very poor emulsion.
140 mg. cholesterol	250 mg. cetyl sulphate	Excellent emulsion.

Schulman and Rideal<sup>4</sup> injected compounds of the type  $C_{12}H_{25}X$  (X = various polar groups) under cholesterol films at an air/water interface, and found that the reactivity of the polar groups X towards the alcoholic group of cholesterol could be placed into the following series:—



That the same order of reactivity towards cholesterol holds at an oil/water interface can be seen from Table IV, the stability of the emulsions being taken as a measure of the stability of the complexes between cholesterol and the various long chain polar compounds ( $C_{16}$  hydrocarbon chains in all cases, except for the bile acids).

TABLE IV.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
100 mg. cholesterol	70 mg. cetyl sulphate	Stability excellent.
100 mg. cholesterol	70 mg. cetyl sulphonate	Stability excellent.
100 mg. cholesterol	70 mg. sodium palmitate	Stability good.
100 mg. cholesterol	70 mg. cetyl trimethyl ammonium bromide	Stability good.
100 mg. cholesterol	70 mg. sodium taurocholate	No emulsion.
100 mg. cholesterol	70 mg. sodium glycocholate	No emulsion.
100 mg. cholesterol	70 mg. sodium desoxycholate	No emulsion.

The emulsions were prepared by hand-shaking.

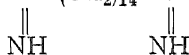
Hexadecylamine was not available for inclusion in the above series. A mixture of the  $C_{17}$  amine and cholesterol did not stabilise "nujol" in water emulsions at all well at pH 7, but gave very good emulsions at pH 2.0. The poor emulsion at pH 7 was, therefore, probably due to the small solubility of heptadecylamine in water at pH 7. A series similar to that shown in Table IV can be obtained, using cetyl alcohol in place of cholesterol. The resulting emulsions, however, are very viscous ("emulsion greases"), and their true stability is rather difficult to determine. The high viscosity of the emulsions is presumably due

<sup>3</sup> Schulman and Hughes, *Biochem. J.*, 1935, **29**, 1243.

<sup>4</sup> Schulman and Rideal, *Nature*, 1939, **144**, 100.

to the formation of *solid* molecular complexes at the oil/water interface, since it is known that cetyl alcohol and many long chain polar compounds form solid complexes at an air/water interface.

The effect of substituting for the long chain polar compound substances containing a polar group at each end of the chain is of great interest. It has been shown that sodium palmitate, for example, rapidly penetrates films such as cholesterol or octadecylamine with the formation of stable complexes. Cockbain and Schulman<sup>5</sup> found, however, that sodium thapsate ( $\text{Na OOC}(\text{CH}_2)_{14}\text{COONa}$ ) penetrated films of octadecylamine at an air/water interface only very poorly, and could readily be squeezed out of the surface to form an adsorbed double layer underneath. In the case of emulsions it is found that sodium palmitate + cholesterol give good emulsions of "nujol" in water, whilst, under the same conditions, sodium thapsate and cholesterol have no emulsifying action. Similarly, Palmityl amidine + cholesterol give fairly good "nujol" in water emulsions under conditions for which cholesterol + palmityl diamidine ( $\text{NH}_2-\text{C}-(\text{CH}_2)_{14}-\text{C}-\text{NH}_2$ ) have no emulsifying action. This contrast



between monopolar and dipolar (polypolar) compounds has important biological implications. The latter compounds adsorb on to protein films, but do not penetrate lipid films. The monopolar compounds penetrate lipid films readily.

### Effect of Concentration of the Emulsifying Agent on Emulsion Stability.

The stability of an emulsion is a function of the size of the dispersed droplets. Other things being equal, emulsions containing large droplets will separate rapidly, and emulsions containing small droplets will separate only slowly. There is plenty of evidence that oil droplets of about  $4\mu$  diameter (covered with an adsorbed layer of emulsifying agent) are sufficiently small to separate only slowly. Suppose, then, that a stable emulsion is to be prepared of 10 c.c. of "nujol" in 40 c.c. of water, using cholesterol + cetyl sulphate as the emulsifying agent. The quantity of cholesterol required will be two-thirds the amount necessary to cover 10 c.c. of "nujol" dispersed into droplets of  $4\mu$  diameter, with a monolayer of cholesterol, providing that all the cholesterol in the system goes to the oil/water interface. This quantity is 16 mg. The factor  $\frac{2}{3}$  is put in because the "nujol" droplets contain an equimolecular complex of cholesterol and cetyl sulphate at the interface and a cetyl sulphate molecule occupies  $20 \text{ \AA}^2$  as compared with  $40 \text{ \AA}^2$  for a cholesterol molecule. That the above deductions are correct is shown in a very striking manner by the experiments described below.

A series of emulsions of "nujol" (10 c.c.) in water (40 c.c.) was prepared, emulsification being produced by hand-shaking for 15 seconds. In every case 75 mg. of cetyl sulphate were dissolved in the water whilst varying quantities of cholesterol were dissolved in the "nujol." The reason for taking 75 mg. of cetyl sulphate will be explained later. It was found that with 25 mg. of cholesterol a very good emulsion was obtained, whilst with 12.5 mg. of cholesterol the emulsion was very poor. 50 mg. or more of cholesterol resulted in emulsions only a little more stable than that

<sup>5</sup> Cockbain and Schulman, *Trans. Faraday Soc.*, 1939, **35**, 716.

obtained with 25 mg. of cholesterol. This is shown in Fig. 1, where emulsion stability is plotted against the concentration of cholesterol. On the basis of the above calculations 32 mg. of cholesterol could cover 10 c.c. of "nujol" dispersed into particles of about  $2\mu$  diameter, with 8 mg. of cholesterol the particles would have to be about  $8\mu$  diameter. It can be seen that stable emulsions are obtained as soon as sufficient cholesterol is used to cover "nujol" droplets between 3 and  $4\mu^*$  diameter with a monomolecular film (a mixed film with cetyl sulphate).

With a mixture of cetyl sulphate and cholesterol as emulsifying agent, more cetyl sulphate than cholesterol should be required in order to obtain stable emulsions. Schulman and Stenhagen<sup>2</sup> showed that an equimolecular complex of cetyl sulphate and cholesterol at an air/water interface collapsed at surface pressures about 8 dynes/cm., but when an excess of sodium cetyl sulphate ( $2 \times 10^{-6}$  g./c.c.) was present in the underlying solution, the complex was stable up to pressures of 48 dynes/cm. Thus an excess of cetyl sulphate underneath the equimolecular cholesterol-cetyl sulphate complex greatly increases the stability of the complex. From Schulman and Stenhagen's results we can calculate the concentration of cetyl sulphate required to stabilise 1 cm.<sup>2</sup> of interface occupied by the equimolecular cholesterol-cetyl sulphate complex. The amount of cetyl sulphate required to stabilise 10 c.c. of "nujol" in 40 c.c. of water when

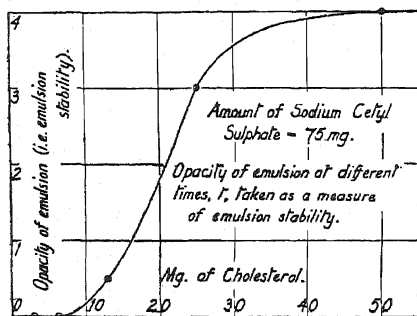


FIG. 1.

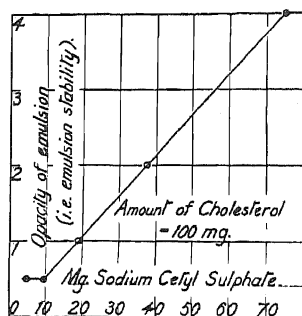


FIG. 2.

the "nujol" is dispersed into particles  $4\mu$  in diameter is calculated to be 58 mg. To test this calculation a series of emulsions of "nujol" (10 c.c.) in water (40 c.c.) was prepared by hand-shaking. In all cases 100 mg. of cholesterol were dissolved in the "nujol" and varying quantities of cetyl sulphate were dissolved in the water. The results are shown in Fig. 2, where the emulsion stability is plotted against amount of cetyl sulphate. With less than 18.5 mg. of cetyl sulphate, no stable emulsions are obtained. Above 18.5 mg. the emulsion stability increases in direct proportion to the amount of cetyl sulphate until the latter is about 75 mg., after which the emulsions are permanent for a long time, and differences are difficult to discern. The agreement between the calculated value of 58 mg. and the observed value of 75 mg. is quite satisfactory. Actually, by calculation, 75 mg. of cetyl sulphate is just sufficient to stabilise the 10 c.c. of "nujol" when present as droplets  $3\mu$  in diameter. The proportionality in Fig. 2 between stability and cetyl sulphate concentration rather suggests that one is stabilising more and more "nujol" droplets of  $3\mu$  diameter until the whole of the "nujol" is stabilised as droplets of this diameter.\* Experimentally the first signs of any emulsion stability were observed with

\* In the stabilised emulsions the maximum number of droplets were of the order  $4.3\mu$  diameter, this fact has also been generally established for oil droplets in stabilised emulsions. Harkins and Muckhergee and King (1939).

18.5 mg. cetyl sulphate which is sufficient to stabilise the "nujol" into droplets of  $12\mu$  diameter. It is of interest that according to Harkins,<sup>6</sup> droplets of this diameter are just small enough to show emulsion properties. The calculated concentration of cetyl sulphate, which, when mixed with cholesterol, was required to stabilise the "nujol" in water emulsions was obtained from Schulman and Stenhagen's data on the stability of a cholesterol-cetyl sulphate complex at an air/water interface. The agreement, therefore, between the calculated and observed concentrations is another confirmation of the close analogy between phenomena occurring at air/water and "nujol"/water interfaces.

### The Stability of "Nujol" in Water Emulsions.

It has been shown in the preceding sections that intermolecular reactions taking place at a "nujol"/water interface are very similar to those which occur at an air/water interface. A detailed knowledge of the latter reactions is now available, so that one can deduce the factors which are important for the stabilisation of "nujol" droplets in water. The one difference between "nujol"/water and air/water interfaces is that "nujol" causes an expansion of liquid films present at the interface. If the interfacial films are brought into a closely packed condensed state, however, all the "nujol" is eliminated from the interfacial monolayer. We may consider a mixture of "nujol" and water; if a substance such as cholesterol or cetyl alcohol is dissolved in the "nujol" there will be a certain aggregation of the molecules at the oil/water interface in accordance with Gibbs' Law, but owing to the solubility of cholesterol or cetyl alcohol in the oil phase, the interfacial tension lowering will not be very large. Similarly, if a water soluble substance such as cetyl sulphate is dissolved in the water phase, the crowding of the molecules at the interface will not be large unless high concentrations of cetyl sulphate are used, e.g. 2 or 3 per cent. Thus we find that cholesterol and similar oil soluble substances do not emulsify "nujol" at all whilst compounds like cetyl sulphate or soaps in high concentration only emulsify "nujol" with difficulty.

The conditions required for the production of stable emulsions are satisfied if complexes of certain types are formed at the oil/water interface. The function performed by such complexes are described below, taking the cholesterol-cetyl sulphate complex as an example.

(1) The complex must consist of at least 2 components, one of which is appreciably soluble in water, and the other appreciably soluble in oil, and the complex must be a stable one. Under these conditions, molecules of both types are held in the interface. The cholesterol cannot pull the cetyl sulphate molecules into the oil phase and the cetyl sulphate cannot pull the oil soluble cholesterol into the water. Since the complex remains stable when formed, only minute concentrations of each component are required to cover the oil/water interface and stabilise the emulsion.

(2) The interfacial tension must be negligibly small, so that the dispersion of the oil in the water phase involves as small an increase in free energy as possible. It has been shown by Schulman and Rideal<sup>7</sup> that stable complexes at an air/water interface lower the surface tension<sup>2</sup> as much as 60 dynes/cm. (for the above-stated example), which is much greater than the surface tension lowering of 40 dynes/cm., or less, pro-

<sup>6</sup> Harkins, *J. Physical Chem.*, 1932, **36**, 98.

<sup>7</sup> Lyons and Rideal, *Proc. Roy. Soc. A*, 1929, **124**, 322.

duced even by the concentrated cetyl sulphate solution at an air/water interface<sup>8</sup> (at the equivalent concentration lowering of the surface tension, is only 22 dynes). The interfacial tension of the soap at an oil/water interface can go down to about 3 dynes/cm., so that, by analogy with the air/water interface results, the interfacial tension of stable complexes at an oil/water interface must be very small indeed. Each component of the complex holds the other component at the interface so that a very high concentration is obtained at the interface.

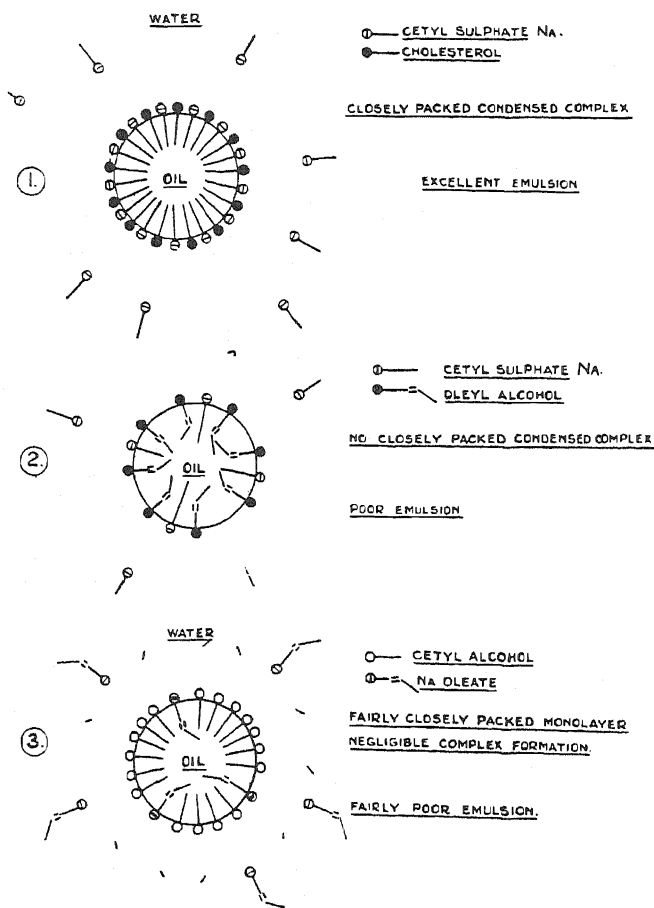


FIG. 3.

(3) In conditions (1) and (2) the stability of the interfacial film and the interfacial tension lowering have both been stressed. These two factors depend markedly on the presence of an excess of the water soluble component under the equimolecular mixed film.

(4) The interfacial film must be a condensed liquid film, condensed because a high interfacial concentration of the complex is necessary, liquid because the film must be easily reformed on distortion.

<sup>8</sup> Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243.

(5) For oil in water emulsions the oil droplets must be electrically charged. In fact, one of the chief actions of the complex is to crowd ions into the interface, since ions on their own repel one another, and thus yielding only vapour films at the interface. It will be shown later that if a complex consisting of 2 neutral molecules is formed at the interface, water in oil emulsions are obtained.

In Fig. 3 is given a diagrammatic representation of the conditions existing at the interface of a stabilised oil droplet ("nujol") in water. Three different complexes which show marked differences in stabilising power are illustrated.

The three diagrams represent the three possible types of stereochemical packing at the interface. More molecules are crowded at the interface in diagram (1) than in (3) than (2). The emulsion stability actually decreases in this order.

### Ease of Formation of Emulsions.

With some emulsifying agents, emulsification of "nujol" in water can be brought about merely by hand-shaking for 2 or 3 seconds. We call this "spontaneous" emulsification. With other agents emulsification can only be produced by using high powdered homogenisers. Whether or not emulsification is spontaneous depends on the interfacial tension  $\sigma$  of the system. If  $\sigma$  is extremely small, e.g. a fraction of dyne per cm., very little energy is required to break up the oil into droplets as small as  $4\mu$  in diameter. Hand-shaking is, therefore, sufficient. If  $\sigma$  is several dynes/cm. a considerable amount of such energy is necessary to disperse the oil into droplets of  $4\mu$  diameter, necessitating the use of an emulsifying machine. Adsorption of the emulsifying agent on to the oil droplets, artificially created by the homogeniser, occurs, the interfacial tension thereby being lowered.

For this adsorption process to be effective large concentrations of soap are necessary. Clearly, the condition of a very low interfacial tension would be of no avail in the easy formation of emulsions if the oil droplets produced immediately coalesced. A second condition can, therefore, be postulated, namely that the interfacial film of emulsifying agent should prevent the coalescence of the droplets. By using an emulsifying agent consisting of 2 components which form a suitable molecular complex at an oil/water interface, the above 2 conditions can be satisfied. As described in the last section, molecular complexes of the type cholesterol-cetyl sulphate present at an oil/water interface lower the interfacial tensions to negligible values and at the same time stabilise the oil droplets. For systems in which molecular complexes are used as emulsifying agents, the conditions required for spontaneous emulsification are the same as the conditions necessary for the production of emulsions of high stability, i.e. the interfacial tension should be very low, the interfacial molecular complex should be stable, and in the liquid condensed state, the oil droplet as a whole should be electrically charged. This charge is obtained by crowding ionic emulsifying agents, by means of a complex, into the interface.

It may be noted that if the molecular complex film is a viscous film, the resulting emulsion is very viscous and grease-like, and vigorous hand-shaking is necessary to form the emulsion, even if the interfacial tension is very low.

It seems possible that the ultimate limit to the size of the oil droplets



present in an emulsion (assuming excess of emulsifying agent is present) is determined by the Brownian movement of the droplets. Certainly, Brownian movement becomes very marked with droplets less than  $0.5\mu$  in diameter, and no stable emulsions could be made containing droplets smaller than this. This diameter is at least ten times greater than that of soap micelles, which are associated molecular complexes. On the above view, it will be seen that living cells bounded by a membrane cannot be expected to be smaller than  $0.5\mu$  in diameter unless the membrane is very rigid. For if they were, Brownian movement would tend to bring about fusion of the cells. The biological significance of this will be mentioned elsewhere.

### Special Complexes.

#### Bile Acids.

It has been found both from film penetration and emulsion stability experiments that the bile acids do not form complexes with long chain alcohols, cholesterol, glycerides or proteins. That they have an affinity for long chain fatty acids is shown by the following experiments. 200 mg. of sodium desoxycholate dissolved in 40 c.c. of water were added to 10 c.c. of oleic acid. A good emulsion was produced on hand-shaking. Good emulsions were also obtained using sodium glycocholate and sodium taurocholate instead of sodium desoxycholate, but no emulsions were obtained with the bile acid salts using "nujol" or long chain glyceride oils. The biological significance of these results will be mentioned elsewhere.

#### Proteins.

The same general rules for oil in water emulsions with protein as the water soluble component of the emulsifying agents can be applied, as already mentioned, for the lipoids.

0.66 per cent. gelatin solution is a poor emulsifying agent for "nujol" but if cholesterol be added to the oil phase a greatly enhanced emulsion is obtained. Similarly, other substances which are known to form complexes with proteins at the air/water interface greatly enhance the emulsion properties of the protein. Thus oleic acid, or elaidic acids, or oleyl alcohol aid the emulsion. There is some evidence that these substances work better than the saturated compounds.

The general order of reactivity of these compounds, as measured by emulsion stability, is the following (with gelatine),

cholesterol > oleic acid > oleyl alcohol > elaidic acid > stearic  
acid > cetyl alcohol.

### Summary.

1. It is shown that molecular interactions occurring at a "nujol"/water interface are closely analogous to the corresponding interactions at an air/water interface which have been widely studied with the Langmuir Trough apparatus.

2. The stability of "nujol" in water emulsions depends on the properties of the interfacial film of emulsifying agent. Optimum stability of the emulsion is obtained under the following conditions: (a) the interfacial film must be electrically charged; (b) the interfacial film must be stable and in the "condensed" state, i.e. as many charged molecules as

possible should be crowded into the interface. In this way, the interfacial tension is reduced to extremely small values.

3. The above two conditions are satisfied when the interfacial film consists of a molecular complex of two suitable substances, one of which is an oil soluble substance and the other an ionisable water soluble substance.

4. The stability of the interfacial complex film is markedly increased by the presence of excess water-soluble molecules above that necessary for a monolayer around the droplets, whereas only a monolayer is necessary for the oil-soluble component (for the cholesterol "nujol" system).

5. The stability of a "nujol" in water emulsion depends markedly on the nature of the two components chosen to form the interfacial complex film. The stability of such films runs parallel with the stability of the same films at an air/water interface, and depends on the van der Waals forces of attraction between the non-polar parts of the two components and on the interaction between the respective head groups. Hence alterations in the size of the non-polar residues, the stereochemical configuration of these residues, the nature of the polar heads, etc., cause alterations in the molecular packing and stability of the interfacial complex films and alterations, therefore, in the stability of the "nujol" in water emulsions, the stability of the emulsion can be deduced from a knowledge of the stability of the corresponding molecular complex at an air/water interface.

Our thanks are due to Professor E. K. Rideal for much help and stimulating discussion, to the Medical Research Council for a personal grant (J.H.S.), and to the I.C.I. Ltd. (Dyestuffs Group) for financial aid (E.G.C.) which made this work possible.

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## MOLECULAR INTERACTIONS AT OIL/WATER INTERFACES.

### PART II. PHASE INVERSION AND STABILITY OF WATER IN OIL EMULSIONS.

BY J. H. SCHULMAN AND E. G. COCKBAIN.

*Received 15th February, 1940.*

In Part I<sup>1</sup> the conditions necessary for the formation of "nujol" in water emulsions were given. Two of the conditions were as follows: (1) the interfacial film must be in the liquid condensed state, and (2) the film must be electrically charged. It will be shown below that in order to produce phase-inversion of such emulsions the electric charge on the oil droplets must first be removed, whereupon the oil in water emulsion breaks. If, in addition, the composition of the aqueous and oil phases is such as to enable a solid condensed film, or, better, an "inter-linked" solid condensed film, to be formed at the interface, then an inversion process occurs with the formation of a water in oil emulsion. This is true for different types of emulsifying agents and over a wide range of conditions.

<sup>1</sup> Schulman and Cockbain, *Trans. Faraday Soc.*, 1939, 35, 716.

### Positively Charged Long-Chain Compounds as Emulsifying Agents.

When heptadecylamine is dissolved in "nujol" (10 c.c.) and shaken with N/100 HCl solution (10 c.c.) an oil in water emulsion is obtained. (The stability of the emulsion is rather poor, as would be expected from the conclusions of Part I.) Table I shows the effect of adding various salts and acids to this oil in water emulsion. The type of emulsion so obtained (oil in water or water in oil) and the nature of the interfacial film at an air/water interface are given. The continuous phase was determined in the usual way by admixture of the emulsion with water or oil and by addition of water-soluble or oil-soluble dyes.

TABLE I.

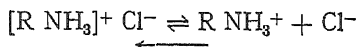
Emulsifying Agents.	Interfacial Film.	Emulsion Type.
(1) Heptadecylamine HCl ( $pH$ 2.0) *	Liquid (charged +) †	Oil in water.
(2) (1) + $(Na_2PO_3)_3$	Solid (neutral)	Water in oil.
(3) (1) + $Na_2SO_4$	Solid (neutral)	Water in oil.
(4) (1) + tannic acid	Liquid (charged +)	Oil in water.
(5) Heptadecylamine + Na tannate ( $pH$ 7 to 8)	Solid (neutral)	Water in oil.
(6) Heptadecylamine + 3N. HCl	Solid (multilayer) Film (neutral)	Water in oil.
(7) Heptadecylamine alone ( $pH$ 7.0)	Amine too soluble in the oil phase to form any emulsion at all.	

\* Charge was determined by Cataphoresis experiments.

† Heptadecylamine HCl films, owing to repulsion between like charges in single component films are really vaporous. On neutralisation of these charges by the polyvalent negative anions the film is solidified, showing that the film is no longer charged.

It can be seen in Table I that when the interfacial film at an air/water interface is solid, water in oil emulsions are obtained. The difference in rigidity of a given film at an air/water and an oil/water interface will be merely one of degree. It can be concluded, therefore, that a rigid, or at least a very viscous, film at the oil/water interface favours the formation of a water in oil emulsion. In example (1) the interfacial film will not only be liquid but also positively charged, owing to the ionisation of the amine hydrochloride. The ionised film molecules will undoubtedly repel one another and have a marked freedom of movement. By the addition of polyvalent negative ions, as in (2) and (3), the positive charge on the amine molecules is neutralised, and two or more of the molecules are inter-linked, depending on the valency of the anions added. The movement of the film molecules is, therefore, restricted, giving a rigid or viscous film. Thus a requirement for the formation of water in oil emulsions is that the interfacial film should be uncharged. The addition of tannic acid in examples (4) and (5) is of great interest. At  $pH$  2.0 an oil in water emulsion is obtained; at  $pH$  7 to 8 a water in oil emulsion. The conversion of one emulsion into the other by a change of  $pH$  was found to be a reversible phenomenon. Cockbain and Schulman showed that at  $pH$  2.0 tannic acid interacts only weakly with long-chain amine films at an air-water interface, the amine film remaining liquid and ionised. This explains why emulsion

(4) in Table I is of the oil in water type. At  $pH$  7 to 8, tannic acid reacts strongly with an amine film, converting it from a liquid to a rigid solid state. Hence emulsion (5) is of the water in oil type. Tannic acid at  $pH$  7 to 8 acts in the same way as a polyvalent negative ion because a *multiple-point* polar interaction occurs with the amine film. Heptadecylamine in "nujol" forms a water in oil emulsion with 3  $N$ . HCl solution. An amine film on 3  $N$ . HCl at an air/water interface is in the viscous liquid or solid state. Actually we consider the film to be a multi-layer film such as is obtained with soap films spread on very alkaline solutions. In addition to the rigidity of the amine film on 3  $N$ . HCl, it is very probable that the diffuse ionisation of the amine hydrochloride is largely suppressed by the high



concentration of chloride ions, so that the interfacial film is uncharged. (These are the conditions in which salting out occurs probably by removal of the diffuse layer by the high ionic concentration and consequent discharging of the micelle on a "mass law" action.) The result is that emulsion (6) is of the water in oil type.

Long-chain quaternary ammonium compounds are too soluble in water and too highly ionised to form other than highly expanded vaporous films at an oil/water interface. Hence, lissolamine (cetyl trimethyl ammonium bromide) in dilute solution has very little emulsifying action on "nujol"/water systems. But if the lissolamine molecules are held in the interface by cholesterol from the oil phase, good oil in water emulsions are obtained as explained in Part I. Table II shows the effect of adding salts or tannic acid to such emulsions.

TABLE II.

Emulsifying Agents.	Interfacial Film.	Emulsion Type.
(1) Lissolamine ( $pH$ 7) *	Lissolamine too soluble in water phase to form an emulsion.	
(2) Lissolamine + cholesterol ( $pH$ 7)	Liquid condensed (charged +)	Oil in water.
(3) (2) + $Na_2SO_4$	Liquid (charged +)	Oil in water.
(4) (2) + $(NaPO_3)_3$	Solid (neutral)	Water in oil.
(5) (2) + tannic acid ( $pH$ 3)	Solid (neutral)	Water in oil.

\* Charge determined by Cataphoresis experiments.

We conclude that divalent sulphate ions are unable to neutralise the charge on the highly ionised quaternary ammonium salt, or to rigidly interlink the lissolamine molecules. These processes do occur in the presence of trivalent phosphate ions over a wide  $pH$  range, and in the presence of tannic acid at  $pH$  3. The marked differences between heptadecylamine (Table I) and lissolamine (Table II) are probably not due entirely to differences in the degree of ionisation. Thus, the presence of three methyl groups round the nitrogen atom in lissolamine might hinder association between the positively charged lissolamine molecules at the interface and polyvalent anions in the aqueous phase. It has been established experimentally that in mixed films of quaternary ammonium salts and long-chain alcohols, complex formation is strongly

inhibited by steric factors connected with the quaternary ammonium group. No steric hindrance effects are observed when a long-chain amine is substituted for the quaternary ammonium compound.

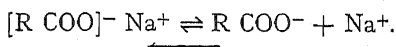
In the case of oil in water emulsions, a stable interfacial film was produced by using an emulsifying agent consisting of two suitable long-chain molecules which formed a complex. With water in oil emulsions, the use of *two* long-chain compounds should not, in general, be necessary, since rigid and uncharged interfacial films can be produced by the association of a single long-chain compound with polyvalent ions of the opposite charge present in the aqueous phase.

### Negatively Charged Soaps as Emulsifying Agents.

When negatively charged soaps are employed as emulsifying agents, the conditions necessary for the production of water in oil emulsions are the same as those formulated in the previous section. These conditions are:—

- (1) The interfacial films should be uncharged.
- (2) The film should be rigid, or at least very viscous.

The above requirements are fulfilled when long-chain carboxylic acid molecules are inter-linked at an oil/water interface by polyvalent metal ions. It is well known that oil in water emulsions stabilised by negatively charged long-chain carboxylates are inverted to water in oil emulsions by the addition of Ca or Ba salts, for example. Similarly, when "nujol" in water emulsions are stabilised by a complex of cholesterol and sodium cetyl sulphate or cholesterol and sodium palmitate, addition of Ba or Ca salts produces a phase inversion. At an air/water interface, liquid complex films of cholesterol + sodium cetyl sulphate (or sodium palmitate) turn solid on injection of Ba or Ca salts into the underlying solution. Sodium palmitate alone will normally give an emulsion of "nujol" in water. On addition of strong caustic soda to this emulsion, inversion occurs at  $pH > 14$ . It is probable that the diffuse ionisation of the sodium palmitate is suppressed by the strong caustic soda, so that the interfacial soap film is largely uncharged,



In addition, the interfacial film is probably solid, since it has been shown that soap films spread on strongly alkaline solutions at an air/water interface are solid multilayer films.<sup>2</sup> The inversion of Na palmitate emulsions at very high  $pH$  values is exactly analogous to the inversion of heptadecylamine emulsions at very low  $pH$  values. Addition of aluminium or thallous salts to "nujol" in water emulsions stabilised by a cholesterol-Na palmitate mixture produces inversion of the emulsions. It is interesting that thallous salts, which are *monovalent*, give water in oil emulsions. It is known, however, that monovalent thallous (or silver) soaps are unionised. Furthermore, they would almost certainly form solid films.

Since the polyvalent metal soaps are insoluble in water or "nujol" (except, perhaps, aluminium soaps at high temperatures), the corresponding water in oil emulsions cannot be prepared directly, but must be produced by an inversion process.

<sup>2</sup> Bikerman, *Proc. Roy. Soc., A*, 1939, 170, 131.

### Direct Preparation of Water in Oil Emulsions.

To obtain directly a water in oil emulsion it is necessary to bring the emulsifying agent to the oil/water interface, so as to form a film which is uncharged and rigid. A very good example is the use of digitonin plus cholesterol as the emulsifying agent. Digitonin is a *neutral* molecule readily soluble in water, and has no emulsifying action by itself on "nujol"/water systems. Nor has cholesterol any emulsifying action by itself. But if an aqueous solution of digitonin is added to a solution of cholesterol in "nujol," excellent water in oil emulsions are obtained. The cholesterol and digitonin are both held at the oil/water interface owing to strong complex formation, giving a rigid and uncharged interfacial film. At an air/water interface, cholesterol-digitonin complexes form very rigid films indeed.

If an acid saponin is used in place of the digitonin, "nujol" in water emulsions are obtained. This is because acid saponins are negatively charged molecules and the acid saponin-cholesterol complex formed at the oil/water interface will also be negatively charged. In addition, it is known that acid saponin-cholesterol complexes at an air/water interface form viscous liquid but not rigid films.

If, in the above experiments, cholesterol acetate or cholesterol stearate be substituted for the cholesterol, hardly any emulsification occurs. As already described in Part I, this is due to the fact that no molecular complexes are formed between cholesterol esters and saponin or digitonin.

A general characteristic of water in oil emulsions is that under the microscope the water droplets have irregular shapes. They appear to be contained in "sacks." We attribute this appearance to the rigid nature of the film surrounding the water droplets, the film molecules being fixed as in a 2-dimensional crystal. Osmotic forces might cause alterations in the shape of the "sacks."

On the other hand, all oil in water emulsions which we have examined contain completely spherical droplets, owing to the interfacial film being in the liquid condensed state. With a liquid interfacial film, the oil droplets could easily regain their spherical shape after being deformed in any way.

### The Mechanism of the Phase Inversion Phenomenon.

In emulsions of oil in water, the interfacial film is in the liquid condensed state, and is electrically charged. The fact that the water is the continuous phase must mean that the oil droplets are electrically charged; since water, being an ionising medium, enables charged oil droplets to repel one another,\* owing to the formation of a diffuse layer or ionic atmosphere around the oil droplets, so that a stable oil in water emulsion can be obtained (providing that the physical characteristics of the interfacial film fulfil the conditions set out in Part I<sup>1</sup>). If, however, the oil were the continuous phase, the fact that the interfacial film consisted of charged molecules could not prevent the dispersed water droplets from coalescing because oil being a non-ionising medium, no electrical diffuse layer or ionic atmosphere can be built up. If, furthermore, the charged interfacial film were an interlinked solid, no coalescence would be likely to occur because of mechanical reasons (see

\* See Theory of *G* Potentials.

requirements for stable water in oil emulsions). However, the above film would not be a rigid interlinked solid, since films consisting of charged molecules are either liquid or gaseous, but not interlinked, owing to repulsion between the molecules in the film. Fig. 1a shows diagrammatically, oil droplets dispersed in water and stabilised by a liquid condensed mixed film such as cholesterol + sodium cetyl sulphate. The adsorbed diffuse double layer of sodium cetyl sulphate is also represented, and the oil droplets are given a negative charge because of the negatively charged cetyl sulphate ions.

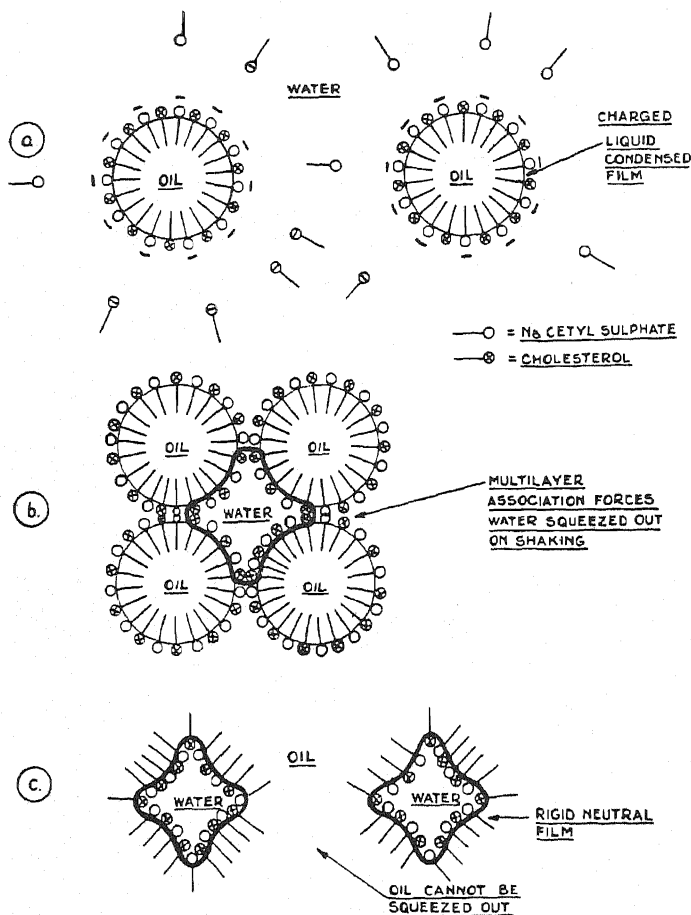


FIG. 1.

In Fig. 1b is shown the state of affairs after polyvalent kations ( $\text{Ca}^{++}$  or  $\text{Ba}^{++}$ , for example) have been added to the oil in water emulsion. Adsorption of the kations has destroyed the negative charge on the oil droplets, thus allowing them to coalesce, the diffuse double layer of sodium cetyl sulphate having been removed by kations in the process.

During the process of coalescence, water molecules can be squeezed out from between the oil droplets very readily because the interfacial film molecules have a strong tendency to align themselves with their

polar heads together, as in their normal crystal packing (see diagram, Fig. 2).

In this connection it is significant that, in the Langmuir-Blodgett technique for obtaining multilayers on metals, the conditions required to produce film deposition are analogous with those necessary for the formation of water in oil emulsions. In film deposition, the molecules of the multilayer are known to be oriented in the normal crystal packing arrangement shown in Fig. 2. Thus, the Ca salt of a long-chain fatty acids or the phosphate salt of a long-chain amine is deposited in double lattice form when built up as a multilayer on metals. The same substances stabilise water in oil emulsions. The reason for the film deposition and for the coalescence of oil droplets covered by an uncharged interfacial film is that water is so readily squeezed out from between the polar heads of the film molecules enabling them to take up their normal crystal packing arrangement.

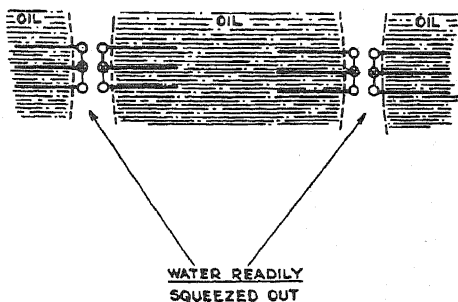


FIG. 2.

Fig. 1*b* shows a number of oil droplets in the coalesced state after removal of the charge on the oil droplets. If, now, the interfacial film is rigid and especially if a cross-linking of the film molecules has occurred to give the crystal packing arrangement described above, the water "sacks" enclosed by the coalesced oil droplets will themselves be stabilised, and will float away. This process is represented in Fig. 1*c*. The emulsion is now of the water in oil type and the interfacial film molecules have their long hydrocarbon chains directed outwards from the water "sacks." No coalescence of these water "sacks" will occur, because the oil cannot be squeezed out from between them. On the contrary, the hydrophobic chains of the film molecules will adhere to the oil molecules of the continuous phase just as ionic head groups in interfacial films adhere to water molecules in emulsions of the oil in water type. Water "sacks" of irregular shape are typical of all water in oil emulsions, the irregular shape being due to the necessary rigidity of the interfacial film.

### Summary.

1. Emulsions of *water in "nujol"* are obtained when emulsifying agents are added which form interfacial films possessing certain characteristics. These are (a) the interfacial film should possess no electric charge; and (b) it should possess considerable rigidity. Thus, water containing digitonin when added to "nujol" containing cholesterol, forms a *water in oil* emulsion directly. Similar behaviour is shown when water is added to "nujol" containing palmitic acid plus heptadecylamine.

2. *Oil in water* emulsions are inverted to *water in oil* emulsions if they are treated in such a way as to make the interfacial film fulfil the above two conditions. Addition of polyvalent ions to oil in water emulsions stabilised by a complex of the opposite charge produces two effects: (a) the interfacial film is discharged enabling the oil droplets to coalesce by a squeezing out



of the water between the interfaces of the oil droplets; (b) a marked increase in the rigidity of the interfacial film is brought about through an interlacing of the film molecules by the polyvalent ions. In this way water "sacks" dispersed in oil are obtained. The water sacks do not coalesce on approach because of the strong affinity between the hydrocarbon chains of the interfacial films and the surrounding oil medium which prevents the oil being squeezed out from between approaching water sacks.

3. The above conditions required for the formation of *water in oil* emulsions are similar to those necessary for the production of multilayers on metals using the Langmuir-Blodgett technique.

4. In place of polyvalent ions, charged molecules containing many polar groups capable of multiple point interaction with the film-forming substance can be used. Thus addition of tannic acid to oil in water emulsions stabilised by a complex containing long chain amines or other positive long chain ions produces an inversion of the emulsion at a suitable  $pH$  value for the interaction.

Our thanks are due to Professor E. K. Rideal for much help and stimulating discussion, to the Medical Research Council for a personal grant (J.H.S.), and to the I.C.I. Ltd. (Dyestuffs Group) for financial aid (E.G.C.) which made this work possible.

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## STUDIES OF THE STRUCTURES OF SOME INORGANIC PENTAHALIDE MOLECULES IN THE VAPOUR PHASE, BY ELECTRON DIFFRACTION.

BY H. A. SKINNER AND L. E. SUTTON.

*Received 27th March, 1940.*

The structural form of some inorganic pentahalides has been the object of recent investigations. Braune and Pinnow<sup>1</sup> have examined  $PF_5$  and  $IF_5$  using the method of electron diffraction by the vapours. They concluded that  $PF_5$  is best represented by a regular trigonal bipyramid structure. It was impossible from the electron diffraction results to assign any definite structure to the  $IF_5$  molecule, but it was shown that the I—F distance is uniform. More recently, Brockway and Beach<sup>2</sup> have reinvestigated  $PF_5$  by the electron diffraction method, and their results, considered together with the observed zero dipole moment in this compound,<sup>3</sup> show conclusively that  $PF_5$  has a regular trigonal bipyramid structure. Ewens and Lister<sup>4</sup> investigated the structure of  $MoCl_5$  using electron diffraction by the vapour. Their examination favoured the trigonal bipyramid structure. The Raman spectra of liquid and solid  $PCl_5$  have been studied by Moureu, Magat,

<sup>1</sup> Braune and Pinnow, *Z. physikal. Chem.*, B, 1937, 35, 239.

<sup>2</sup> Brockway and Beach, *J.A.C.S.*, 1938, 60, 1836.

<sup>3</sup> Linke and Rohrmann, *Z. physikal. Chem.*, B, 1937, 35, 256.

<sup>4</sup> Ewens and Lister, *Trans. Faraday Soc.*, 1938, 34, 1358.

and Wetroff,<sup>5</sup> who concluded that in the liquid state,  $\text{PCl}_5$  has the trigonal bipyramid structure, and that in the solid state, the molecule is a complex ionic structure. Powell, Clarke and Wells<sup>6</sup> from the X-ray crystallographic examination of  $\text{PCl}_5$ , have shown that the ions in the crystal are  $[\text{PCl}_4]^+[\text{PCl}_6]^-$ . Rouault and Schomaker<sup>7(a), (b)</sup> from electron diffraction studies of  $\text{PCl}_5$  in the vapour phase, conclude that the molecule is a trigonal bipyramid, but that there are two distances for the P—Cl links, differing by about 0.10 Å. The pentahalides  $\text{NbBr}_5$ ,  $\text{NbCl}_5$ ,  $\text{TaBr}_5$  and  $\text{TaCl}_5$  have now been investigated in the vapour state by the method of electron diffraction. The results show that the above compounds are best represented by the regular trigonal bipyramid model. The molecule  $\text{NbBr}_5$  is particularly suitable for electron diffraction study, since in this molecule there is little disparity in scattering power between the metal-halogen and halogen-halogen terms. The complete evidence now available would indicate that the inorganic pentahalides as a class have the same structural form—namely that of the regular trigonal bipyramid.

### Experimental.

The chlorides of Nb and Ta were prepared by the action of pure dry  $\text{Cl}_2$  on the powdered metals at a temperature of about 250° C. The compounds were purified by repeated sublimation in a stream of pure dry nitrogen. The bromides of the metals were also prepared by the direct method. The  $\text{Br}_2$ , carefully purified from  $\text{Cl}_2$ , and dried, was passed in a dry  $\text{N}_2$  stream over the powdered metals at about 300° C. The bromides were purified by sublimation in a dry  $\text{N}_2$  stream. It was found necessary to purify the  $\text{NbBr}_5$  more completely by sublimation *in vacuo*. The manipulation of the compounds was carried out in a dry  $\text{N}_2$ -filled box, because of the extreme sensitivity of the compounds to the moisture of the air.

The diffraction patterns from the vapours of the compounds were photographed in the apparatus described by de Laszlo.<sup>8</sup> The photographs were taken with the following oven temperatures:

$\text{TaCl}_5$ . . .	160-180° C.	$\text{NbCl}_5$ . . .	150-170° C.
$\text{TaBr}_5$ . . .	180-200° C.	$\text{NbBr}_5$ . . .	200-230° C.

The camera distance was 28.05 cm., and the electron wave-lengths about 0.06 Å.

### Electron Diffraction by Niobium Pentabromide.

The photographs for this compound showed five maxima, whose intensities appeared to decrease fairly regularly with increasing diameter. The rings appeared to be symmetrical with the exception of the third maximum which shaded off markedly towards the outside, and gave the appearance of a shelf in between the third and fourth maxima. The shelf was not sufficiently distinct to allow of accurate measurement.

The observed  $s_0$  ( $= 4\pi \frac{\sin \theta/2}{\lambda}$ ) values, and the visually estimated intensities of the maxima, are given in Table I. The positions of the maxima and minima were measured visually on a comparator. The  $C$  values given in Table I, are the "weighted" intensities of the maxima, calculated by the method of Schomaker and Degard.<sup>9</sup> The  $C$  values

<sup>5</sup> Moureu, Magat and Wetroff, *C.R.*, 1937, **205**, 276.

<sup>6</sup> Powell, Clarke and Wells, *Nature*, 1940, **145**, 149.

<sup>7</sup> (a) Rouault, *C.R.*, 1938, **207**, 620; (b) Schomaker, reported in Pauling, *Nature of the Chemical Bond*, 1939, footnote, p. 103.

<sup>8</sup> de Laszlo, *Proc. Roy. Soc., A*, 1934, **146**, 662.

<sup>9</sup> Degard and Schomaker, *J.A.C.S.*, in press.

TABLE I.

Max.	Min.	I.	C.	S <sub>obs.</sub>	S <sub>A</sub> .	S <sub>B</sub> .	S <sub>C</sub> .	S <sub>D</sub> .	l <sub>A</sub> .	l <sub>B</sub> .	l <sub>O</sub> .	l <sub>D</sub> .
1		10	10	(3.29)	3.57	2.80	3.14	3.58	(2.496)	—	—	(2.503)
				—	—	3.50	—	—	—	—	—	—
				—	—	4.17	—	—	—	—	—	—
	1			(4.80)	5.02	5.12	4.16	4.98	(2.405)	(2.453)	—	(2.386)
2		10	18	5.81	6.28	6.17	5.97	6.07	2.486	2.443	—	2.403
	2			6.99	7.40	7.38	6.85	7.75	2.435	2.428	—	2.550
				—	—	—	7.58	—	—	—	—	—
				—	—	—	8.20	—	—	—	—	—
3		7	12	7.95	8.43	8.46	9.02	8.83	2.439	2.448	—	2.555
				—	9.32	9.37	—	—	—	—	—	—
				—	9.88	10.00	—	—	—	—	—	—
	3			10.02	10.68	10.78	10.90	9.85	2.451	2.474	—	—
				—	—	—	—	10.85	—	—	—	—
				—	—	—	—	11.30	—	—	—	—
4		6	5	10.93	11.75	11.90	11.80	12.14	2.473	2.504	—	2.555
				12.25	13.08	13.07	12.93	13.36	2.456	2.454	—	2.508
5	4	3	1	13.25	14.20	14.10	14.55	14.40	2.465	2.448	—	2.500
Mean									2.458	2.457	—	2.512
Average deviation									0.014	0.018	—	0.042
Final value									Nb—Br 2.46 ± 0.03 A.			

are obtained by multiplying each of the visually estimated intensities by the factor  $s_0^2 \cdot \exp. (-as_0^2)$ , where  $a$  is chosen so that the coefficient of the strongest ring is ten times that of the weakest.

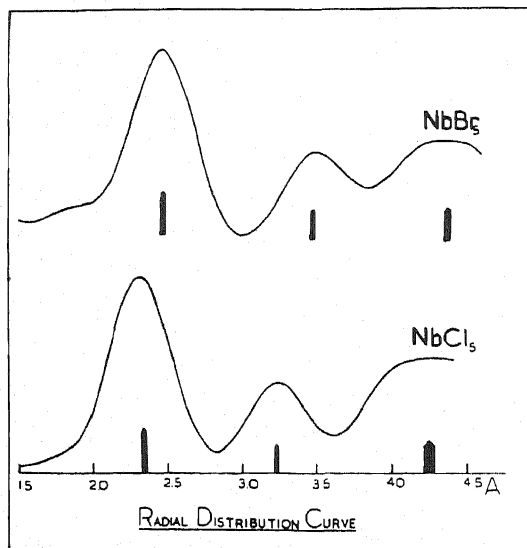


FIG. 1.

The radial distribution curve, calculated from the observed  $s$  values, and the  $C$  values, is reproduced in Fig. 1. This curve shows peaks at distances corresponding to

Nb—Br = 2.46 A.  
and Br—Br = 3.51 A.

From these values it follows that there are a number of Br—Nb—Br angles of  $90^\circ$ .

Assuming a uniform Nb—Br distance of 2.30 A. four models were investigated by the correlation method. The choice of this distance merely affects

the scale, and not the form of the theoretical scattering curves, so that the true value of the assumed distance may subsequently be obtained by simple proportion from the observed and calculated  $s$  values.

The models investigated are described below:

**Model A.** The Br atoms occupy the corners of a regular trigonal bipyramid, with the Nb atom at the centre.

**Model B.** The Br atoms at the corners of a square pyramid with the Nb atom at the centre of the base.

Both models A and B have a number of Br—Nb—Br angles of  $90^\circ$ , according to the requirements of the radial distribution results.

**Model C.** A regular planar model, with all the Br—Nb—Br angles =  $72^\circ$ .

**Model D.** The Br atoms at the corners of a square pyramid, with the Nb atom centrally placed *above* the square base, so that the angle Br—Nb—Br is  $105^\circ$ .

The theoretical scattering curves for each of the above models are reproduced in Fig. 2.

The qualitative differences in these four curves are well marked, and the comparison of curves C and D with the general appearance of the plates is itself sufficient to rule out the corresponding models.

Curve C has an unsymmetrical second maximum, and a shelf on the inside of the third maximum. The plates showed the shelf on the outside of the third maximum, and the second maximum was quite symmetrical.

Curve D is unsatisfactory in the regions of the second and third minima, and the fourth maximum. The shading off (shelf) occurs on the inside of the fourth maximum so that the third minimum would lie nearer to the third maximum than to the fourth, whereas the plates show the third minimum to be displaced distinctly towards the fourth maximum.

The most marked difference in the curves A and B lies in the first maximum. Whereas curve A has a perfectly symmetrical first maximum, curve B has it clearly split into two parts. The plates obtained from

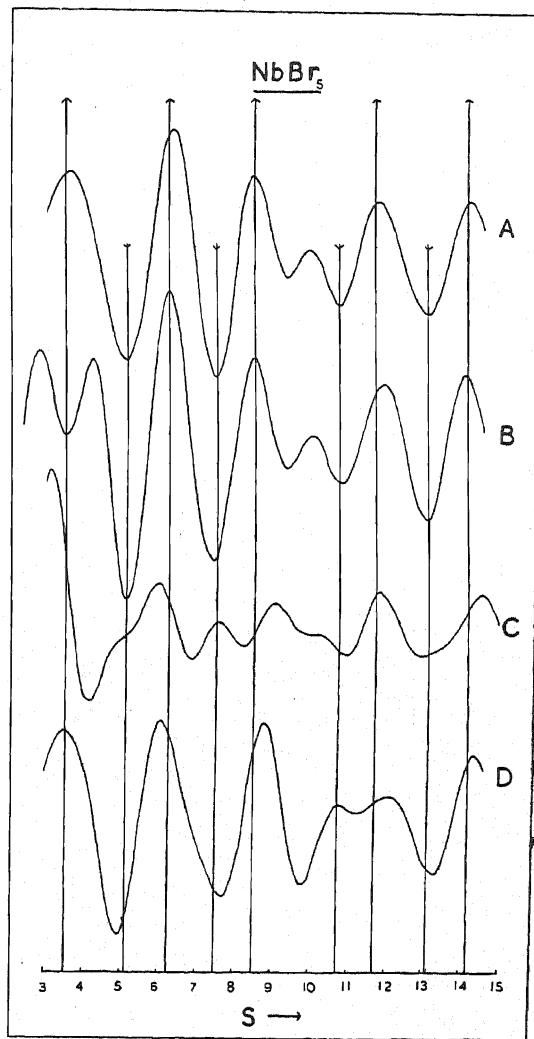


Fig. 2.

$\text{NbBr}_5$  were exceptionally clean and distinct and there was absolutely no indication of any disymmetry or splitting in the first maximum. The qualitative comparison of the theoretical curves with the photographic plates, definitely favours Model A (the trigonal bipyramid) and would certainly rule out Models C and D. Model B is incompatible with the observed first maximum. Although it is unwise (as a general rule) to rely upon the appearance of the first maximum, it is felt that such a marked difference in the first maximum, as that required by models A and B, would be observable on the plates.

Table I gives the  $s$  values for the four calculated curves and the distances of the Nb—Br link derived from these values (*i.e.*,  $2.30 \cdot s_{\text{calc.}}/s_{\text{obs.}}$ ) in the various models. This table shows that the best quantitative agreement is given by curve A, although this is only slightly better than that of curve B.

It would be expected that the models A and B should give theoretical scattering curves similar to one another, since both models have a number of Br—Nb—Br angles of  $90^\circ$ , and consequently have many of the Br—Br distances equal. Model B is likely to be less stable than Model D, because in the latter the weighted mean of the Br—Br distances is  $3.77 \text{ \AA}$ , as compared with  $3.86 \text{ \AA}$  in the former, and the potential energy of repulsion between the Br atoms is

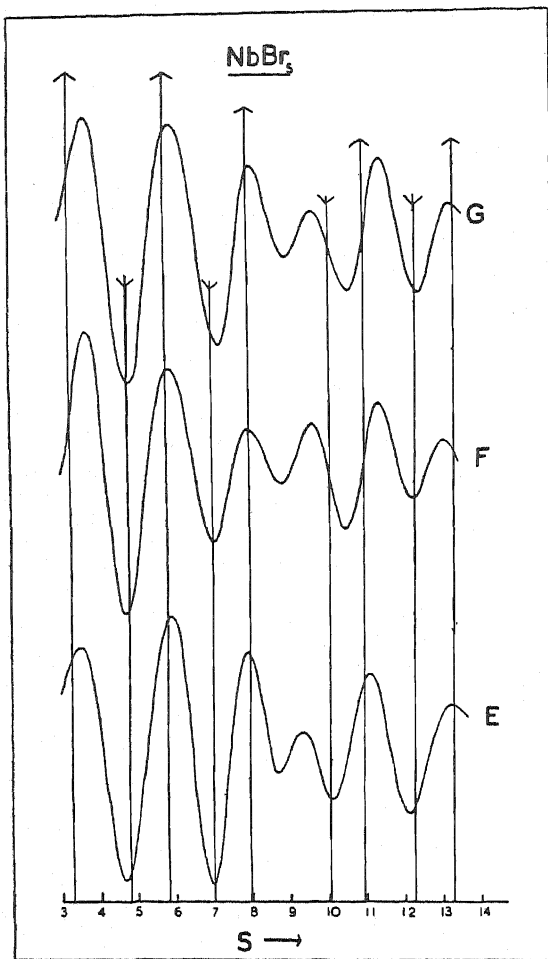


FIG. 3.

larger. Consequently, although the model B is in good agreement with the electron diffraction results (except in the unreliable region of the first maximum), it is in itself a less likely structure than model D—which has been shown to be far less in agreement with the experimental results than model A. It may therefore be concluded that of the models considered, the most satisfactory is the regular trigonal bipyramid, with a Nb—Br distance =  $2.46 \pm 0.03 \text{ \AA}$ .

In view of the reported variation of the lengths of the P—Cl bonds in  $\text{PCl}_5$ ,<sup>7(a), (b)</sup> it was deemed necessary to consider some trigonal bipyramid

models with unequal distances. Three such models were therefore examined by the correlation method, the theoretical scattering curves for which are shown in Fig. 3. The models were all of the trigonal bipyramid type, with dimensions as follows:

Model E.	{Nb—Br (apices) = 2.50 A.
	{Nb—Br (base) = 2.40 A.
Model F.	{Nb—Br (apices) = 2.60 A.
	{Nb—Br (base) = 2.30 A.
Model G.	{Nb—Br (apices) = 2.50 A.
	{Nb—Br (base) = 2.30 A.

The curves for models E and G agree closely with the curve for model A, in general form, and are less satisfactory only in that the shelf on the out-

TABLE II.

$s_{\text{obs.}}$	$s_E$	$s_F$	$s_G$	$s_E/s_{\text{obs.}}$	$s_F/s_{\text{obs.}}$	$s_G/s_{\text{obs.}}$
(3.29)	3.53	3.70	3.71	(1.073)	(1.125)	(1.128)
(4.80)	4.70	4.66	4.79	(0.979)	(0.971)	(0.998)
5.81	5.90	5.87	5.98	1.015	1.010	1.029
6.99	7.00	6.99	7.17	1.001	1.000	1.026
7.95	7.92	7.89	8.09	0.996	0.992	1.018
10.02	10.16	10.47	10.58	1.014	1.045	1.056
10.93	11.14	11.34	11.48	1.019	1.038	1.055
12.25	12.20	12.27	12.43	0.996	1.002	1.015
13.25	13.23	13.04	13.29	0.998	0.984	1.003
Mean				1.006	1.010	1.028
Average deviation				0.009	0.018	0.015

side is more marked in these models. The curve for model F is definitely unsatisfactory, since this model would have the shelf clearly measurable, and the intensities of the maxima do not follow closely the intensities estimated from the plates.

The quantitative comparison of these curves shows that in all three cases the agreement is not as good as that given by model A; but the quantitative agreement of curve E is sufficiently close to make a definite choice between the models E and A impossible.

The measured  $s$  values and the values of the  $s_{\text{calc.}}/s_{\text{obs.}}$  ratios for the models E, F, and G are given in Table II. The average deviations from the mean values of these ratios for all the models considered are given subsequently.

Model A is therefore in the best quantitative agreement, but the agreement is only slightly better than in model E. It is therefore not possible to state that in  $\text{NbBr}_3$  all the Nb—Br links are of the same length, although it can be stated that the link lengths do not deviate from the mean value (2.46 Å) by more than  $\pm 0.05$  Å.

TABLE IIa.

Model.	Average Deviation $s_{\text{calc.}}/s_{\text{obs.}}$
A . . .	0.006
B . . .	0.008
C . . .	—
D . . .	0.018
E . . .	0.009
F . . .	0.018
G . . .	0.015

### Electron Diffraction by Niobium Pentachloride.

The photographs for this compound showed five rings, the intensities of each decreasing regularly with increasing diameter. The maxima appeared symmetrical with the exception of the third which fell away slowly on the outside. The observed  $s$  values and intensities are given in Table III.

The radial distribution curve, reproduced in Fig. 1, showed strong peaks at distances corresponding to the internuclear distances:

$$\text{Nb—Cl} = 2.29 \text{ \AA.} \quad \text{Cl—Cl} = 3.23 \text{ \AA.}$$

From these values it follows that there are a number of Cl—Nb—Cl angles of  $90^\circ$ .

Assuming a Nb—Cl distance of 2.00 Å., three models were investigated by the correlation method. These models were similar to those described for  $\text{NbBr}_5$ .

**Model A.**—Regular trigonal bipyramid.

**Model B.**—Square pyramid, Cl—Nb—Cl angles =  $90^\circ$ .

**Model C.**—Planar model.

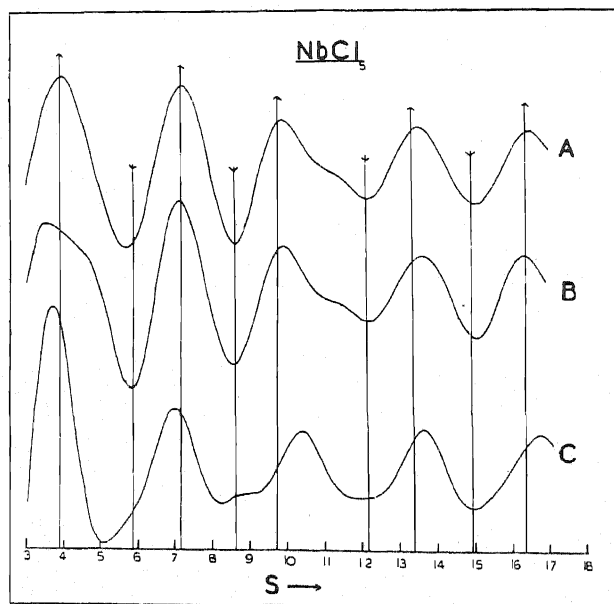


FIG. 4

The theoretical intensity curves derived from these three models are shown in Fig. 4.

Curve C is unsatisfactory: it shows no sign of the observed shading off of the third maximum on the outside, instead this appears on the inside. Curves A and B are very similar except in the region of the first maximum. The appearance of this on the plates was perfectly symmetrical, and there was no sign of the dysymmetry that curve B shows. Quantitatively, the best agreement is given by model A, although the agreement is only slightly better than that of model B. The quantitative agreement of model C is poor, and the planar model can be definitely ruled out.

On the whole, the experimental evidence is more in favour of model A than of model B, and furthermore, the considerations of the stability of model B, described under  $\text{NbBr}_5$ , apply equally in the chloride. The

s values for the three calculated curves, and the Nb—Cl distances derived from these values (*i.e.*  $2.00 \cdot s_{\text{calc.}}/s_{\text{obs.}}$ ), are given in Table III.

The value found for the Nb—Cl distance is  $2.29 \pm 0.03$  Å.

TABLE III.

Max.	Min.	I.	C.	$s_{\text{obs.}}$	$s_{\text{A.}}$	$s_{\text{B.}}$	$s_{\text{C.}}$	$l_{\text{A.}}$	$l_{\text{B.}}$	$l_{\text{C.}}$
<b>Niobium Pentachloride.</b>										
1		10	10	(3.39)	3.93	3.50	3.70	(2.319)	(2.065)	(2.183)
	1			(5.11)	5.62	5.79	5.00	(2.200)	(2.266)	(1.957)
2		10	19	6.25	7.14	7.07	6.94	2.285	2.262	2.237
	2			7.52	8.53	8.53	8.20	2.269	2.269	2.181
3		7	12	8.48	9.83	9.86	10.32	2.318	2.325	2.434
	3			10.62	12.11	12.13	11.94	2.281	2.284	2.249
4		4	4	11.67	13.42	13.54	13.56	2.300	2.320	2.324
	4			13.02	14.98	15.00	14.87	2.301	2.304	2.284
5		3	1	14.26	16.40	16.24	16.67	2.300	2.278	2.338
Mean . . . .								2.293	2.293	2.292
Average deviation . .								0.013	0.021	0.062

Final value : Nb—Cl =  $2.29 \pm 0.03$  Å.

**Tantalum Pentabromide.**

1		10	10	(3.12)	3.37	3.08	3.23	(2.484)	(2.270)	(2.381)
	1			(4.80)	4.66	5.03	4.32	(2.233)	(2.410)	(2.070)
2		10	22	5.85	6.23	6.14	6.08	2.449	2.414	2.390
	2			7.03	7.54	7.40	7.12	2.467	2.421	2.329
3		8	20	7.97	8.56	8.50	9.13	2.470	2.453	2.635
	3			9.88	10.47	10.60	10.17	2.437	2.468	2.367
4		6	10	11.04	11.50	11.80	11.92	2.396	2.458	2.483
	4			12.32	13.16	13.02	13.00	2.457	2.431	2.427
5		3	3	13.37	14.38	14.13	14.50	2.474	2.431	2.494
	5			14.68	15.60	15.35	15.74	2.444	2.405	2.466
6		3	1	15.84	17.00	17.44	16.88	2.468	2.532	2.451
Mean . . . .								2.451	2.446	2.449
Average deviation . .								0.020	0.028	0.065

Final value : Ta—Br =  $2.45 \pm 0.03$  Å.

**Tantalum Pentachloride.**

1		10	10	(3.18)	3.86	3.78	3.73	(2.428)	(2.377)	(2.346)
	1			(5.09)	5.40	5.65	5.30	(2.122)	(2.220)	(2.083)
2		10	24	6.16	7.10	7.05	6.97	2.305	2.289	2.263
	2			7.51	8.65	8.56	8.48	2.304	2.280	2.258
3		6	16	8.58	10.00	9.95	10.30	2.331	2.319	2.401
	3			10.44	11.95	11.95	11.77	2.289	2.289	2.255
4		3	6	11.57	13.24	13.46	13.50	2.289	2.327	2.334
	4			13.02	14.95	14.96	14.89	2.296	2.298	2.287
5		1	1	14.28	16.52	16.32	16.62	2.314	2.286	2.328
Mean . . . .								2.304	2.298	2.304
Average deviation . .								0.011	0.014	0.043

Final value : Ta—Cl =  $2.30 \pm 0.02$  Å.



## Electron Diffraction by Tantalum Pentabromide.

The photographs for this compound showed six rings, the intensities of each decreasing with increasing diameter. The maxima appeared to

be symmetrical with the exception of the third which fell off slowly towards the outside. The  $s$  values and measured intensities are given in Table III. The radial distribution curve (reproduced in Fig. 5) showed strong maxima at distances corresponding to

$$\text{Ta—Br} = 2.47 \text{ \AA.}$$

$$\text{Br—Br} = 3.45 \text{ \AA.}$$

From these values it follows that there are a number of Br—Ta—Br angles of  $90^\circ$ .

Assuming a Ta—Br distance of 2.30 \AA., three models were studied by the correlation method. The models were similar to those chosen in the investigation of  $\text{NbBr}_5$ .

Model A—regular trigonal bipyramid.

Model B—square pyramid, Br—Ta—Br angles =  $90^\circ$ .

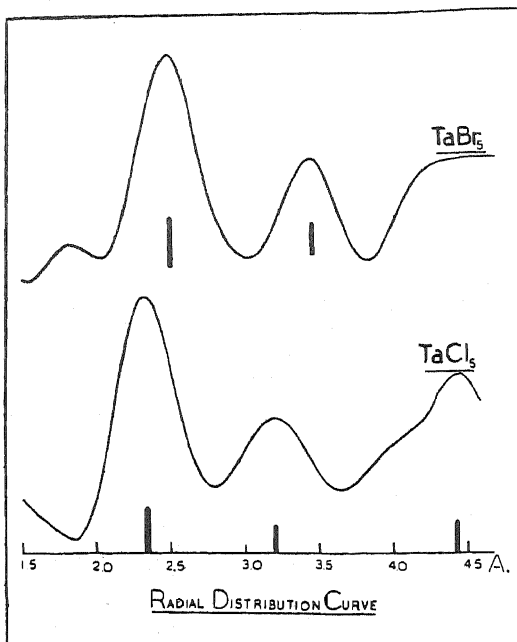


FIG. 5.

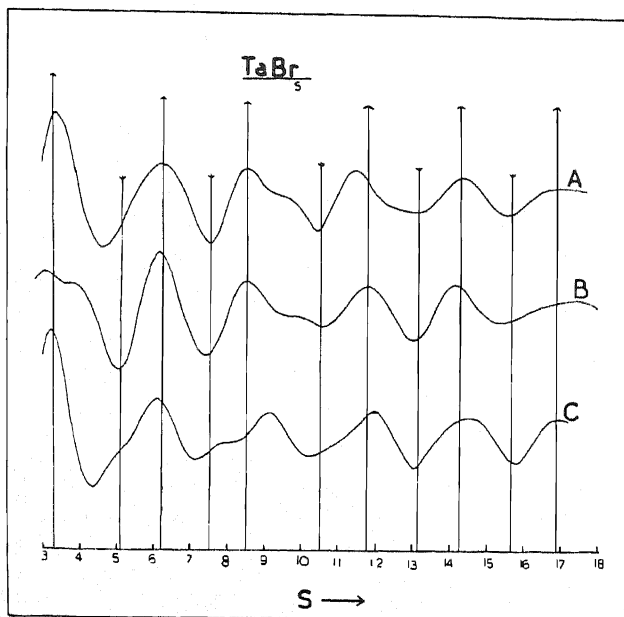


FIG. 6.

Model C—planar model.

The theoretical scattering curves for these three models are shown in Fig. 6.

The appearance of curve C at once suggests that the planar model is impossible. This curve is unsatisfactory in the regions of the third maximum and the second and third minima. The shading off of the third maximum appears on the inside in curve C, whereas the plates show the shelf on the outside. The only appreciable difference in curves A and B occurs in the first maximum. The plates showed the first maximum to be quite symmetrical, and there was no sign of the shelf which model B would require. Quantitatively, curve A is slightly better than curve B, and very much better than curve C. The experimental evidence, therefore, favours model A rather than model B, and rules out model C completely.

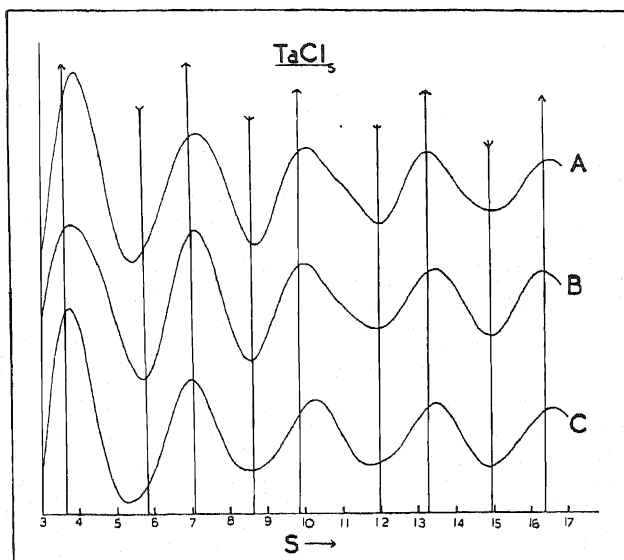
The  $s$  values for the three calculated curves, and the Ta—Br distances derived from these values (*i.e.*,  $2.30 \cdot s_{\text{calc.}}/s_{\text{obs.}}$ ) are given in Table III.

The value for the Ta—Br distance was found to be  $2.45 \pm 0.03$  Å.

### Electron Diffraction by Tantalum Pentachloride.

The photographs for this compound showed five rings, the intensities of which decreased fairly regularly with increasing diameter. The maxima

FIG. 7.



appeared symmetrical with the exception of the third, which fell away more slowly on the outside, the succeeding minimum falling nearer the fourth maximum.

The observed  $s$  values and estimated intensities are given in Table III.

The radial distribution curve is reproduced in Fig. 5, and showed peaks at distances corresponding to

$$\text{Ta—Cl} = 2.32 \text{ Å. and Cl—Cl} = 3.20 \text{ Å.}$$

Assuming a Ta—Cl distance of 2.00 Å., three models were investigated by the correlation method, similar to those chosen in the previous pentahalide investigations:

**Model A**—regular trigonal bipyramid.

**Model B**—square pyramid, with Cl—Ta—Cl angles =  $90^\circ$ .

**Model C**—planar model.

The theoretical scattering curves derived from the above three models are shown in Fig. 7.

Curve C is unsatisfactory in the region of the third minimum—there is no indication of the observed shading off of the third maximum, with consequent displacement of the third minimum towards the fourth maximum.

The general form of the two curves A and B is almost identical, and it is impossible in this compound to choose between the models A and B from either qualitative or quantitative comparison of the curves.

The  $s$  values for the three calculated curves, and the derived Ta—Cl distances (*i.e.*  $2.00 \cdot s_{\text{calc.}}/s_{\text{obs.}}$ ) are given in Table V.

The best value for the Ta—Cl distance is  $2.30 \pm 0.02$  Å.

Two further trigonal bipyramid models, in which the distances Ta—Cl were not assumed to be uniform, were investigated by the correlation method. The models had the dimensions :

**Model E.** Ta—Cl (apices) = 2.35 Å.

Ta—Cl (base) = 2.25 Å.

**Model F.** Ta—Cl (apices) = 2.40 Å.

Ta—Cl (base) = 2.20 Å.

The scattering curves for these models are in all essentials similar to the curve for model A, and are not reproduced. The quantitative agree-

TABLE IV.

$s_{\text{obs.}}$	$s_E$	$s_F$	$s_E/s_{\text{obs.}}$	$s_F/s_{\text{obs.}}$
(3.18)	3.40	3.46	(1.069)	(1.088)
(5.09)	4.83	4.86	(0.949)	(0.955)
6.16	6.19	6.20	1.005	1.006
7.51	7.49	7.52	0.997	1.001
8.58	8.68	8.74	1.012	1.018
10.44	10.47	10.78	1.003	1.033
11.57	11.76	11.92	1.016	1.030
13.02	13.00	13.01	0.998	0.999
14.26	14.30	14.12	1.001	0.989
Mean . . .			1.005	1.011
Average deviation . . .			0.006	0.014

limits of  $2.30 \pm 0.05$  Å., and the *average* bond length must be 2.30.

The  $s$  values, and the  $s_{\text{obs.}}/s_{\text{calc.}}$  ratios for the curves E and F are given in Table IV.

### Discussion.

The electron diffraction investigation of the four pentahalides described in this paper shows that in all cases the most satisfactory representation of the structure is the trigonal bipyramid. The only alternative form compatible with the experimental results is the square pyramid described as model B. Because of the greater repulsion between bromine atoms, this model is less stable than model D, which is, however, not acceptable on experimental grounds. A conclusive choice between the models A and B could be made from measurements of the dipole moments of these compounds. In the case of  $\text{PF}_5$ , the dipole moment of the vapour has been measured and found to be zero—so

that in this compound the trigonal bipyramid is the only acceptable structure.

It would appear that the trigonal bipyramid form is general for the class of compounds of the type  $MX_5$ . This structure has been shown to obtain also in such mixed pentahalides<sup>10</sup> as  $PF_3Cl_2$ , and substituted pentahalides<sup>11</sup> as  $Me_3SbX_2$ . The general stereochemical form of the pentahalides suggests a common bond orbital type existing in these compounds. The problem of directed valency in 5-co-ordinated compounds has been recently treated by Kimball,<sup>12</sup> from the group theory point of view. This author concludes that the trigonal bipyramid form occurs when bond orbitals of the types  $sp^3d$  and  $spd^3$  are employed, and that the square pyramid structural form should be found with bond orbitals of the types  $sp^2d^2$ ,  $sd^4$ ,  $p^3d^2$  and  $pd^4$ . The valence configuration  $d^5$  has the bonds directed along the slant edges of a pentagonal pyramid.\* The possible valency configurations for the relevant Group 5 elements, and their characteristics, are summarised in the following table:—

*Phosphorus Pentahalides.*

Neon core . . . .	3s 3p 3d		
(10)	2 222 2	$sp^3d$	Trig. Bi-pyr.

*(a) Niobium, (b) Tantalum pentahalides.*

(a) Krypton core . . .	Penultimate <i>d</i>	Ultimate			
		<i>s</i>	<i>p</i>	<i>d</i>	
(36) . . . .	22222	0	000		$d^5$ Pentagonal Pyramid.
	02222	2	000		$sd^4$ Sq. Pyr.
	00222	2	200		$spd^3$ Trig. Bi-pyr.
	00022	2	220		$sp^2d^2$ Sq. Pyr.
(b) Hafnium core . . .	00002	2	222		} $sp^3d$ Trig. Bi-pyr.
	00002	2	222		
	00000	2	222	2	

Orbital theory in its present state enables us to say only that the first  $sp^3d$  arrangement for the niobium and tantalum pentahalides is more likely than the second, because the *d* levels must be less stable in the ultimate group than in the penultimate group. No definite choice between the remaining five states can be made. The experimentally observed trigonal bipyramid structures in these compounds indicates, however, that the  $spd^3$  or  $sp^3d$  valency configurations are preferred.

As was explained in the experimental section, the question as to

<sup>10</sup> Brockway and Beach, *J.A.C.S.*, 1938, 60, 1836.

<sup>11</sup> A. F. Wells, *Z. Krist.*, 1938, 99, 367.

<sup>12</sup> G. E. Kimball, *J. Chem. Physics*, 1940, 8, 194.

\* The pentagonal pyramid structure has not been considered in the experimental section for any of the pentahalides. There is no doubt, however, that this structural form will not be in agreement with the diffraction results. The halogen-metal-halogen angles in such a structure must be less than  $72^\circ$ , and the radial distribution results indicate that at least some of these angles are approximately  $90^\circ$ .

whether the metal-halogen links in the niobium and tantalum pentahalides are of uniform length, or vary in a similar manner to the reported variation in the link distances in phosphorus pentachloride, cannot be conclusively answered. The diffraction results show that the length of a metal-halogen link in the niobium and tantalum pentahalides does not vary from the experimentally determined link length in the regular trigonal bipyramid model by more than  $\pm 0.05$  Å., and that the average length of the M—X link is that determined in the regular trigonal bipyramid model.

The bond lengths in the niobium and tantalum pentahalides are about 0.10 Å. shorter than the normal covalent bond lengths for these compounds. There is some uncertainty in the normal covalent radii of Nb and Ta, and the values taken here are the metallic radii. (Goldschmidt values for co-ordination number six.)

Compound.	Observed M-X Distance.	Metal Atom Radius (in Å).	Calc. M-X Distance (in Å).	Per Cent. Shortening.
NbBr <sub>5</sub> . .	2.46 $\pm$ 0.03	1.40	2.54	3.2 %
NbCl <sub>5</sub> . .	2.29 $\pm$ 0.03	1.40	2.39	4.2 %
TaBr <sub>5</sub> . .	2.45 $\pm$ 0.03	1.40	2.54	3.5 %
TaCl <sub>5</sub> . .	2.30 $\pm$ 0.02	1.40	2.39	3.8 %

The contraction of the links in these compounds is of the same order of magnitude as the contractions observed in MoCl<sub>5</sub> and IF<sub>5</sub>, and not quite as great as that in PF<sub>5</sub>.

### Summary.

The structures of niobium and tantalum pentabromides and pentachlorides in the vapour phase have been investigated by electron diffraction. The compounds have the trigonal bipyramid structure, and the observed bond lengths are :

Nb—Br =  $2.46 \pm 0.03$ , Nb—Cl =  $2.29 \pm 0.03$  : Ta—Br =  $2.45 \pm 0.03$  : and Ta—Cl =  $2.30 \pm 0.02$  Å.

The significance of the experimental results has been discussed.

The authors are indebted to Professor N. V. Sidgwick, F.R.S., for his interest and advice, to the Department of Scientific and Industrial Research for a maintenance allowance to one of them (H.A.S.), to the Royal Society for the loan of an electric calculating machine, and to Imperial Chemical Industries Ltd. for a grant towards the cost of the research.

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# STUDIES OF THE STRUCTURES OF BISMUTH CHLORIDE AND BROMIDE MOLECULES IN THE VAPOUR PHASE, BY ELECTRON DIFFRACTION.

BY H. A. SKINNER AND L. E. SUTTON.

*Received 27th March, 1940.*

The structure of several of the trihalides of the Group 5B elements have been determined, and give a series of experimental results, whose eventual interpretation should be of considerable importance in the elucidation of the cause or causes of the shortening of metal-halogen links. The diffraction experiments with the bismuth halide vapours were undertaken to complete further the investigated structures of the Group 5B trihalides.

## Experimental.

Bismuth bromide was prepared by passing a stream of pure dry  $N_2$  carrying pure dry  $Br_2$  vapour, over a sample of pure metallic Bi, at about  $250^\circ$ . The compound was purified by repeated sublimation in a dry  $N_2$  stream.

Bismuth chloride was prepared by the direct action of pure dry  $Cl_2$  on heated metallic Bi, and purified by repeated sublimation in a stream of dry nitrogen.

The diffraction by the compounds was studied in the apparatus described by de Laszlo.<sup>1</sup>

The samples of the compounds were contained inside a pyrex tube within a copper oven. The best oven temperatures for photographing the patterns from the vapours were found to be  $BiBr_3$  at  $220^\circ$ - $230^\circ$  C., and  $BiCl_3$  at  $220^\circ$ - $230^\circ$  C.

## Diffraction by Bismuth Bromide.

Nine plates were measured, each showing five maxima, which appeared to be symmetrical. The first two rings were very intense, the other three appeared to decrease in intensity

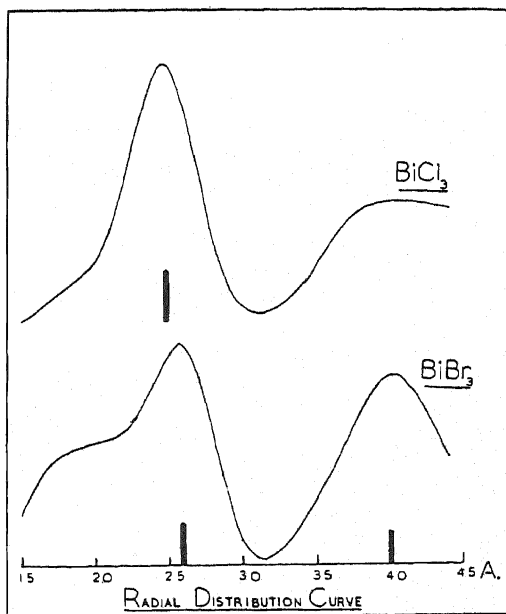


FIG. 1.

<sup>1</sup> de Laszlo, *Proc. Roy. Soc., A*, 1934, 146, 662.

regularly with increasing diameter. The observed  $s$  values and the estimated intensities of the maxima are given in Table I. The radial

TABLE I.

Max.	Min.	$I$ .	$s_{\text{obs.}}$	$s_{90^\circ}$	$s_{98^\circ}$	$s_{102^\circ}$	$s_{106^\circ}$	$s_{112^\circ}$
1		10	(3.44)					
	1		4.35					
2		9	5.25	5.45	5.30	5.27	5.22	5.30
	2		6.67					
3		5	7.87	7.70	8.00	7.96	7.87	7.78
	3		9.11					
4		3	9.99	10.40	10.18	10.16	10.35	10.35
	4		10.40					
5		1	12.26	12.58	12.86	12.75	12.60	12.60

distribution curve, calculated from these values, is reproduced in Fig. 1. This showed peaks at distances corresponding to Bi—Br = 2.58 Å., and Br—Br = 4.02 Å. These values indicate that bismuth bromide has a

pyramidal structure, with the Br—Bi—Br angle =  $101^\circ$ .

Assuming this to be the correct model, and allotting a value of 2.60 Å. to the Bi—Br distance, five theoretical scattering curves were calculated, for models in which the Br—Bi—Br angle varied ( $90^\circ$ ,  $98^\circ$ ,  $102^\circ$ ,  $106^\circ$  and  $112^\circ$ ).

These curves are reproduced in Fig. 2. They do not differ from one another markedly in general appearance, and it is not possible to choose any one model from qualitative comparison alone, although the curves for the angles  $106^\circ$  and  $112^\circ$  are comparatively unsatisfactory in the region of the second maximum. The quantitative agreement is best for the curves of the models with angles  $98^\circ$  and  $102^\circ$ , and the general appearance of these curves is in very good agreement with the plates. The  $s$  values of the maxima and minima of the five calculated curves

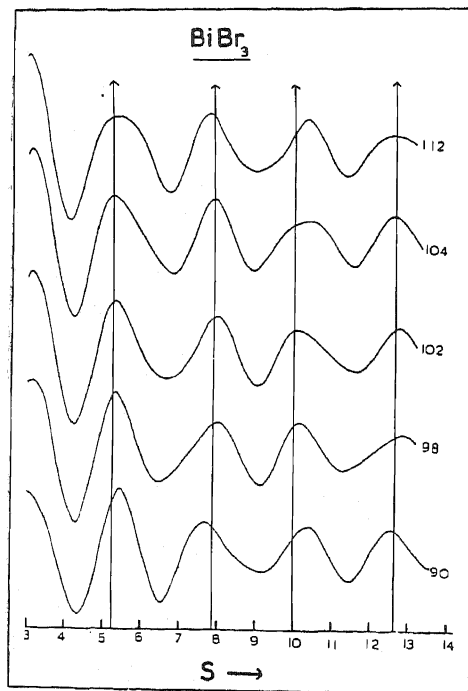


FIG. 2.

are listed in Table I. The Bi—Br distances derived from the  $s$  values of the maxima (*i.e.*,  $2.60 \cdot s_{\text{calc.}}/s_{\text{obs.}}$ ) are given in Table II. From these tables it is seen that the best quantitative agreement is given by the models with Br—Bi—Br angles of  $98^\circ$  and  $102^\circ$ , with the Bi—Br distance of 2.63 Å. The model finally chosen is therefore taken as

$$\text{Bi—Br} = 2.63 \pm 0.02 \text{ Å.}$$

$$\widehat{\text{Br—Bi—Br}} = 100 \pm 4^\circ.$$

## Diffraction by Bismuth Chloride.

Six plates showing five rings were measured. The rings appeared to be symmetrical and decreased in intensity with increasing diameter, the first two rings being considerably more intense than the others.

TABLE II.

Max.	$I_{90^\circ}$	$I_{96^\circ}$	$I_{102^\circ}$	$I_{108^\circ}$	$I_{112^\circ}$
2	2.70	2.62	2.61	2.58	2.62
3	2.54	2.64	2.63	2.60	2.57
4	2.71	2.65	2.64	2.69	2.69
5	2.59	2.65	2.63	2.60	2.60
Mean	2.63	2.64	2.63	2.62	2.62
Av. dev.	0.07	0.01	0.01	0.04	0.04

Best value : Bi—Br =  $2.63 \pm 0.02$  A.

Br— $\widehat{\text{Bi}}$ —Br angle =  $100 \pm 4^\circ$ .

molecule is a triangular pyramid with  $\text{Cl—}\widehat{\text{Bi}}\text{—Cl} = 111^\circ$ .

Assuming this model to be correct, five models were examined by the

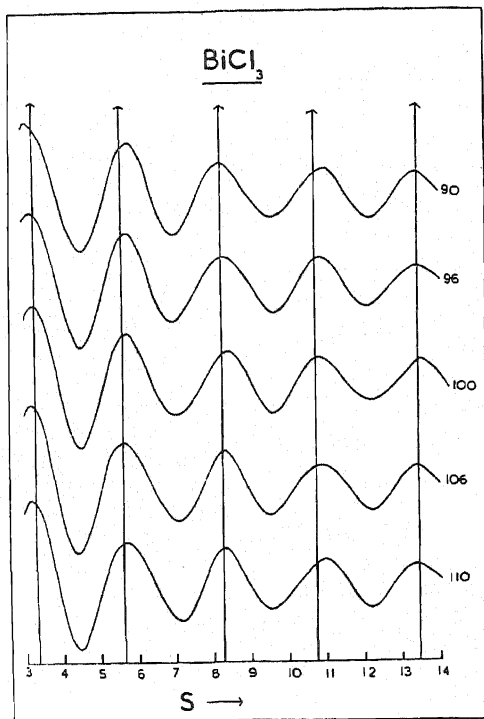


FIG. 3.

correlation method. In each model, the Bi—Cl distance was assumed to be 2.45 A., and the angle was varied ( $90^\circ$ ,  $96^\circ$ ,  $100^\circ$ ,  $106^\circ$  and  $110^\circ$ ). The theoretical scattering curves for these models are reproduced in Fig. 3.

The curves are very similar to one another in general form, and no choice between the models can be made from the qualitative examination alone.

The  $s$  values of the maxima and minima of the calculated curves are given in Table III, and the Bi—Cl distances derived from these values in Table IV.

The quantitative comparison gives the best model the dimensions :

Bi—Cl =  $2.48 \pm 0.02$  A.

and

$\text{Cl—}\widehat{\text{Bi}}\text{—Cl} = 100^\circ \pm 6^\circ$ .



TABLE III.

Max.	Min.	I.	$s_{\text{obs.}}$	$s_{90^\circ}$	$s_{96^\circ}$	$s_{100^\circ}$	$s_{106^\circ}$	$s_{110^\circ}$
1		10	(3.32)	3.12	3.22	3.23	3.20	3.20
	1		(4.64)					
2		9	5.62	5.78	5.72	5.68	5.66	5.78
	2		6.99					
3		5	8.26	8.24	8.35	8.40	8.33	8.30
	3		9.69					
4		3	10.72	11.00	10.88	10.80	10.90	10.95
	4		12.16					
5		1	13.43	13.40	13.45	13.50	13.40	13.40

TABLE IV.

Max.	$l_{90^\circ}$	$l_{96^\circ}$	$l_{100^\circ}$	$l_{106^\circ}$	$l_{110^\circ}$
1	(2.30)	(2.38)	(2.38)	(2.36)	(2.36)
2	2.52	2.49	2.48	2.47	2.52
3	2.44	2.48	2.49	2.50	2.46
4	2.51	2.49	2.49	2.49	2.50
5	2.44	2.45	2.46	2.44	2.44
Mean .	2.48	2.48	2.48	2.48	2.48
Av. dev.	0.04	0.01	0.01	0.02	0.03

Therefore, the best values are :

$$\text{Bi}-\text{Cl} = 2.48 \pm 0.02 \text{ \AA.} \quad \text{Cl}-\widehat{\text{Bi}}-\text{Cl} \pm 100 \pm 6^\circ.$$

### Conclusion.

The bismuth-halogen link distances in the two halides are almost the normal link distances given by the sum of the covalent radii :

Compound.	Observed Bi-X.	Calculated.	% Contraction.
$\text{BiCl}_3$	$2.48 \pm 0.02 \text{ \AA.}$	2.50 \text{ \AA.}	0.8 %
$\text{BiBr}_3$	$2.63 \pm 0.02 \text{ \AA.}$	2.65 \text{ \AA.}	0.75 %

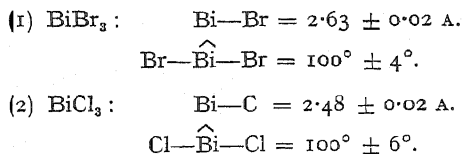
it is found that for the same halogen attached to different central atoms the percentage shortening decreases from P to Sb. In accordance with this rule, the percentage shortening in the Bi halides is less than in the corresponding Sb halides, where the corresponding values are 1.25 % and 1.2 %.

The bond angles of  $100^\circ$  measured in the bismuth halides agree closely with those in the antimony and arsenic halides.

The slight contractions observed are to be anticipated from extrapolation of those already observed in the Group 5B trihalides, where

### Summary.

The structures of bismuth tribromide and trichloride have been investigated by the electron diffraction method. Both compounds have a pyramidal structure, with the dimensions:



The authors are indebted to the Royal Society for the loan of a calculating machine, to Imperial Chemical Industries Ltd. for a grant towards the cost of the research, and to the Department of Scientific and Industrial Research for a maintenance allowance to one of them (H.A.S.).

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## THE ULTRA-VIOLET ABSORPTION AND CHEMICAL CONSTITUTION OF SUBSTITUTED UREAS AND THIOUREAS.

BY ARCHIBALD CLOW AND N. L. HELMRICH.

*Received 17th April, 1940.*

The chemical constitution and diamagnetic susceptibility of a large number of substituted ureas and thioureas have already been investigated by one of the authors<sup>1</sup> who concluded that no static formula would represent the constitution of urea or its derivatives. As the various constitutions deduced from the diamagnetic susceptibilities might have different absorptive powers in the ultra-violet, the present investigation was undertaken to determine whether a parallel could be traced between their constitutions deduced magnetically and their absorption spectra, especially as a short investigation by Rivier and Borel<sup>2</sup> of the absorption spectra of thiourea, trimethylthiourea (normal and *iso*), tetramethylthiourea, dimethyldiphenylthiourea (normal and *iso*) and tetraphenylthiourea indicated that such a parallel did indeed exist. In this discussion the ultra-violet absorption curves between 2200 Å. and 4000 Å. of some 35 urea and thiourea derivatives are correlated with their chemical constitutions. A list of the compounds discussed is given in the experimental part.

The ultra-violet absorption of urea derivatives should be of considerable interest because the different possible constitutions contain a variety of chromophores:  $=\text{C}=\text{O}$ ,  $-\text{NH}_2$ ,  $=\text{C}=\text{S}$ ,  $-\text{S}-\text{H}$ , while the substituents may themselves be chromophoric, *e.g.*, phenyl groups,

<sup>1</sup> Clow, *Trans. Faraday Soc.*, 1937, **33**, 381; 1938, **34**, 457.

<sup>2</sup> Rivier and Borel, *Helv. Chim. Acta*, 1928, **11**, 1219.

or transparent within the range discussed, *e.g.*, methyl or ethyl groups.<sup>3</sup> Practically nothing has been done spectroscopically on urea beyond the researches of Rivier and Borel already mentioned and the various determinations of the absorption of urea and thiourea.<sup>4</sup> Data for the ultraviolet absorption of thio-compounds are equally scanty.<sup>5, 6</sup> Several workers in closely related fields, however, have obtained results of considerable importance. As early as 1913 V. Henri<sup>7</sup> concluded that substances with labile molecules such as urea would absorb strongly in the ultra-violet, but this has been criticised first by Radalescu<sup>8</sup> and subsequently by Ramart-Lucas.<sup>9</sup> Closely related to the absorption of substituted urea derivatives is the work on the absorption of substituted amides and thio-amides by Hantzsch,<sup>10</sup> Amagat,<sup>11</sup> the Freymanns<sup>12</sup> and Ramart-Lucas.<sup>13</sup> The considerable evidence that amides and thio-amides exist in solution in two forms, normal and imido-hydrin, led Hantzsch to investigate the absorption of substituted acid amides and thio-amides on which he showed that (a)  $\text{CCl}_3\text{CONH}_2$  and  $\text{CCl}_3\text{C}(\text{OCH}_3)=\text{NH}$ , (b)  $\text{C}_6\text{H}_5\text{CONH}_2$  and  $\text{C}_6\text{H}_5\text{C}(\text{OC}_2\text{H}_5)=\text{NH}$  have similar continuous absorption curves. From this he concluded that these amides exist, at least partially, in the imido-hydrin form, the absorption of the dimethyl derivative  $\text{C}_6\text{H}_5\text{CONMe}_2$  being quite distinct. These compounds present a close parallel to iso-ureas. It should be noted that a marked solvent effect was displayed by these amides.<sup>14</sup> With regard to the thio-amides  $\text{CH}_3\text{CSNH}_2$  and  $\text{C}_2\text{H}_5\text{CSNH}_2$ , these display strong selective absorption while  $\text{CH}_3\text{C}(\text{SC}_2\text{H}_5)=\text{NH}$  shows weak continuous absorption, from which Hantzsch concluded that the former are true amides. As above, this is relevant to the absorption of iso-thioureas. On account of the conclusions obtained, the study of the absorption curves of mono- and di-substituted diamides<sup>15</sup> is of considerable importance, the presence of the  $-\text{CH}_2-$  group having at least partially the effect of detaching the two chromophores from one another.<sup>16</sup> While  $\text{ArNHCOCH}_2\text{CONH}_2$  and  $\text{ArNHCOCH}_2\text{CONHAr}$  have the same type of absorption curve, the completely substituted compound  $\text{Ar}_2\text{NCOCH}_2\text{CONAr}_2$  is distinctive, being more transparent and only absorbing further into the ultra-violet. Ramart-Lucas concludes, therefore, that the  $\text{ArN}=\text{C}(\text{OH})\text{CH}_2-$  group should have its absorption bands nearer the visible and of greater intensity than those of  $\text{ArNH}-\text{C}(=\text{O})\text{CH}_2-$ , and most of the amides investigated had constitutions corresponding with the first formula. These changes are the same as may take place in substituted ureas.

When the results of the above investigations are applied to the interpretation of the absorption spectra of urea and its derivatives it is found

<sup>3</sup> Ramart-Lucas, *Bull. Soc. Chim.*, 1932, v. I, 289.

<sup>4</sup> (a) Henri and Bielecki, (b) Castille and Ruppel, *Tables Annuelles*, 1930, vii, 789.

<sup>5</sup> Lorenz and Samuel, *Z. physik. Chem.*, B, 1931, 14, 219.

<sup>6</sup> Ley and Arends, *ibid.*, 1932, 15, 311.

<sup>7</sup> Henri, *C.R.*, 1913, 156, 1979.

<sup>8</sup> Radalescu, *Bull. Soc. Sci. de Cluj (Roumania)*, 1928, 4, 297.

<sup>9</sup> Ramart-Lucas, *C.R.*, 1928, 186, 1301.

<sup>10</sup> Hantzsch, *Ber.*, B, 1931, 64, 661.

<sup>11</sup> Amagat, *C.R.*, 1934, 198, 2172.

<sup>12</sup> Freymann and Freymann, *ibid.*, 1936, 202, 1850.

<sup>13</sup> Ramart-Lucas, *Bull. Soc. Chim.*, 1937, v, 4, 478.

<sup>14</sup> Scheibe, *Ber.*, B, 1924, 57, 1330.

<sup>15</sup> Ramart-Lucas, *Bull. Soc. Chim.*, 1934, v, 1, 525.

<sup>16</sup> *Ibid.*, 1932, iv, 51, 289.

that the problem is one of considerable complexity on account of the several factors which influence the absorption. The introduction of substituents which are not themselves chromophores should not, at least in the higher members of a homologous series, influence the absorption,<sup>17</sup> but these same substituents may alter the constitution of the urea molecule to one or other of the possible alternative constitutions with a resulting change in absorption due to the formation of new chromophores within the molecule. The substituent may, however, be chromophoric as in the case of a phenyl group, which possesses a very characteristic selective absorption, and this substituent in addition may, as above, alter the chemical constitution. Further, the presence of two or more chromophores close to one another may exert a mutual influence on the absorption, *e.g.*, the disappearance of the fine bands characteristic of the aromatic ring in all the phenyl substituted ureas discussed, which must be attributed to the chromophore already present in the molecule.

### Experimental.

(a) **Materials.**—The compounds measured were obtained from a variety of sources or were made in the laboratory. Each specimen was subjected to a thorough purification, usually by recrystallisation from pure ethyl alcohol, constancy of melting-point after further purification being taken as the criterion of purity. Those compounds which are liquids were liquid air distilled immediately before use. Wherever possible distilled water was used as the solvent in the determination of the absorption curves, but where the solubility of the substance in water was too small, as in the case of the phenyl derivatives, pure ethyl alcohol was used instead.<sup>18</sup> The solvent used is indicated in the figures. Where the urea or thiourea was a liquid it was measured both as a pure liquid and in solution, though, a micrometer cell not being available, it was not possible to make the comparison over the whole range.

(b) **Methods.**—The spectra were photographed with a Hilger Quartz Spectrograph and Spekker Photometer using tungsten steel electrodes as the source of illumination. The accuracy of the optical system and the transmission of the photometer were checked by examining the absorption spectrum of A.R.  $K_2CrO_4$  which had been recrystallised ten times from distilled water, the absorption curve obtained being in complete agreement with that given by v. Halban and Eisenbrand.<sup>19</sup> The pure liquids were contained in Hilger quartz faced absorption tubes giving layer thicknesses between 1 and 10 mm., while the solutions were contained in 10 cm. tubes. The extinction coefficient was calculated according to the equation  $\log_{10} I_0/I = \epsilon \cdot c \cdot d$ .  $I_0$  and  $I$  being the respective intensities of the incident and transmitted light,  $c$  the concentration in g. mol. per litre,  $d$  the depth of the absorption path in cm. The logarithm of  $\epsilon$  is plotted against the wave-length  $\lambda$  in Å. throughout. The following substances were measured: Urea: N-methyl-urea; N-ethyl-urea; N-phenyl-urea; O-methyl-*iso*-urea; O-ethyl-*iso*-urea hydrochloride; N. N-dimethyl-urea; N. N-diphenyl-urea; N. N'-dimethyl-urea; N. N'-diethyl-urea; N. N'-dimethylol-urea; N. N'-diphenyl-urea; N. N—N'. N'-tetramethyl-urea; N. N—N'. N'-tetraethyl-urea; N. N'-dimethyl-N. N'-diphenyl-urea; N. N'-diethyl-N. N'-diphenyl-urea. Thiourea: N-methyl-thiourea; N-ethyl-thiourea; N-phenyl-thiourea; N-allyl-thiourea; O-methyl-*iso*-thiourea-hydrochloride; N. N-dimethyl-thiourea; N. N-diphenyl-thiourea; N. N'-dimethyl-thiourea; N. N'-diethyl-thiourea;

<sup>17</sup> Ley, *Ber.*, B, 1921, 54, 363.

<sup>18</sup> Clow and Pearson, *Nature*, 1939, 144, 209.

<sup>19</sup> v. Halban and Eisenbrand, *Proc. Roy. Soc., A*, 1927, 116, 160.

N-phenyl-N'-ethylol-thiourea; N,N-dimethyl-N'-phenyl-thiourea; N,N-diphenyl-N'-acetyl-thiourea; N,N-dipropyl-N'-o-tolyl-thiourea; N,N—N',N'-tetramethyl-thiourea; N,N—N',N'-tetraethyl-thiourea; N,N—N',N'-tetraphenyl-thiourea; N,N'-dimethyl-N,N'-diphenyl-thiourea.

### Part I.—Urea Derivatives.

#### Discussion.

(a) **The Absorption of True Carbamides.**—When ureas, in which all four hydrogen atoms had been replaced by alkyl or aryl groups, were

investigated magnetically, an absolute confirmation of their accepted constitution as true carbamides was obtained, consequently it will be advantageous to consider the absorption of these ureas first. From the point of view of diamagnetism it was not necessary, but for the present discussion the tetra-substituted ureas must be divided into two groups, depending on the substituent itself being chromophoric or otherwise. The absorption curves of the tetrasubstituted ureas formed without chromophoric groups are given in Fig. 1, those containing chromophoric groups being discussed with the phenyl ureas. The absorption curves of N,N—N',N'-tetramethyl-urea and N,N—N',N'-tetraethyl-urea reveal that over the

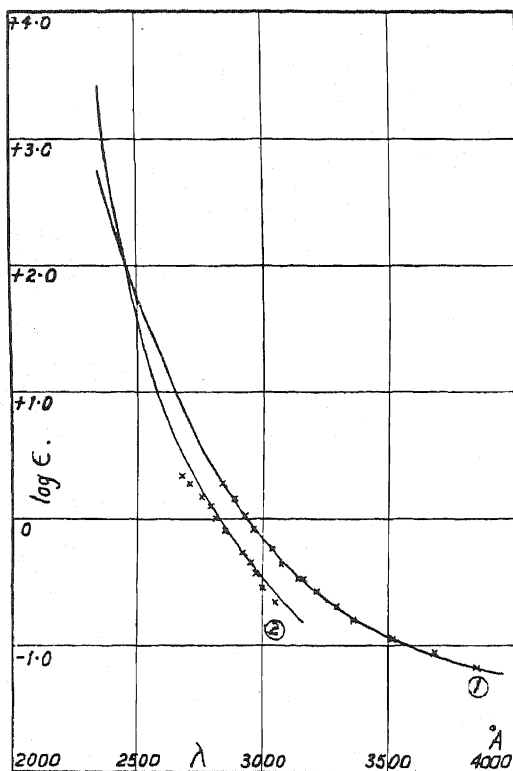


FIG. 1.—(1) N,N—N',N'-tetramethyl-urea.  
(2) N,N—N',N'-tetraethyl-urea.  
x x x pure liquid.  
— soln. in alcohol.

is practically no difference between the absorption of the pure substance and its solution in alcohol. Both tetra-ureas display marked end absorption, the shape of the curves being in marked contrast to the selective absorption characteristic of a compound like acetone containing a single chromophore with a pronounced selective absorption maximum at 2730 Å. The effect of the additional chromophoric groups is evidently to displace this band towards the ultra-violet, as well as to increase the absorption. The introduction of even one —NH<sub>2</sub> group into acetone, giving CH<sub>3</sub>CONH<sub>2</sub>, causes a marked change in the trans-

mission of the molecule,<sup>10</sup> which is also true of urea itself as will be seen in the following section.

**(b) The Absorption of Incompletely Substituted Ureas.**—On substitution a series of changes in the constitution of urea takes place, the extent of the change depending on the nature and position of the substituent. The diamagnetic susceptibility of urea itself suggested that it was a zwitterion which on mono-substitution passed to an equilibrium between the zwitterion and the amino-imino constitution. This was true of N-methyl-urea, N-ethyl-urea and N-propyl-urea, the equilibrium lying in general close to the amino-imino form. The absorption spectra of urea and mono-substituted ureas will be found in Fig. 2, where it will be seen that there is, neglecting the difference in intensity,

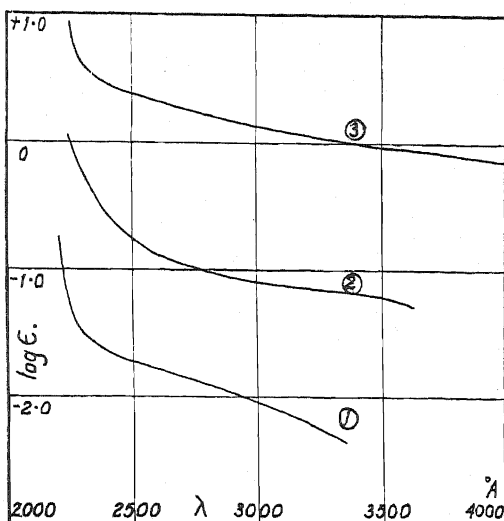


FIG. 2.—(1) Urea.  
(2) N-methyl-urea.  
(3) N-ethyl-urea.  
in water.

a marked similarity between their absorption and that of urea. All display end absorption like the tetra-substituted ureas, but the increased absorption which resulted from complete substitution is very striking, the increase being more than can readily be accounted for simply by

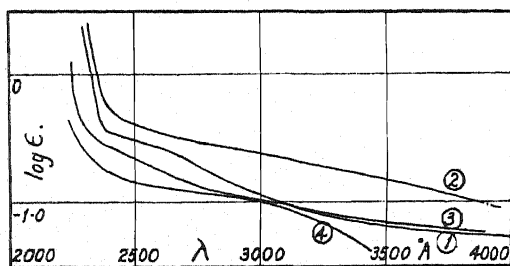


FIG. 3.—(1) N, N-dimethyl-urea.  
(2) N, N'-dimethyl-urea.  
(3) N, N'-diethyl-urea.  
(4) N, N'-dimethylol-urea.  
in water.

the successive introductions of alkyl groups. Indeed the increase in absorption is indubitably suggestive of a change in constitution, and if the structures conforming with the diamagnetic susceptibilities are taken as a guide, an absorption of the type just given would represent the absorption of the urea molecule when its constitution is that either

of a zwitterion or of the amino-imino form.

One of the most important results obtained from the diamagnetic susceptibilities of disubstituted ureas was the difference between the constitutions of N, N and N, N' disubstituted isomers, the weighting effect of both groups attached to one nitrogen being to stabilise the

carbamide constitution. Of the di-substituted ureas only the N, N-dimethyl-urea had a susceptibility approximating to that required for

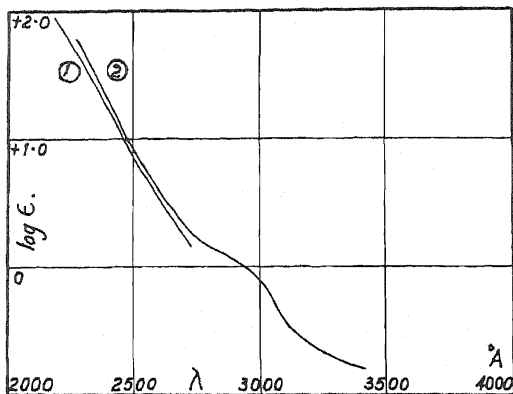


FIG. 4.—(1) O-methyl-iso-urea.  
(2) O-ethyl-iso-urea hydrochloride.  
in water.

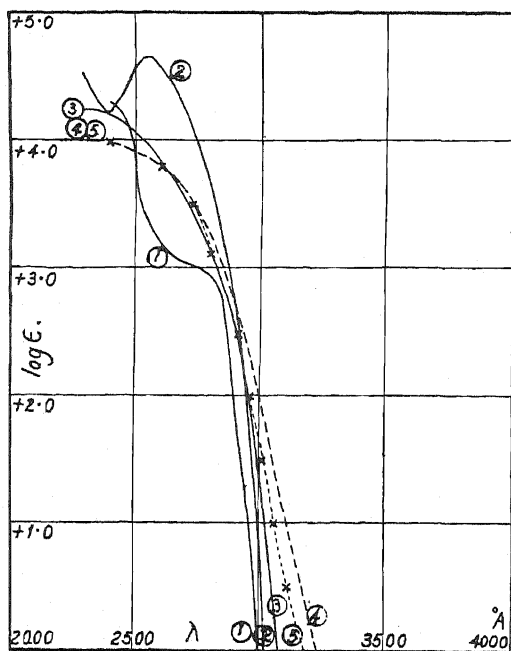


FIG. 5.—(1) N-phenyl-urea.  
(2) N, N'-diphenyl-urea.  
(3) N, N'-diphenyl-urea.  
(4) N, N'-dimethyl-N, N'-diphenyl-urea.  
(5) N, N'-diethyl-N, N'-diphenyl-urea.  
in alcohol.

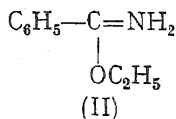
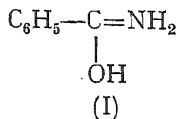
a carbamide constitution. In Fig. 3 are given the absorption spectra of N, N- and N, N'-diethyl-urea, N, N'-dimethyl-urea and N, N'-dimethylol-urea. The resemblance between the various curves is still quite definite, but N, N-dimethyl-urea shows a decided deviation from the general form of these curves between the wavelengths 2400 Å. and 2800 Å. not unsuggestive of the selective absorption of a carbonyl group and in agreement with its diamagnetic susceptibility.

There does not appear to be any obvious correlation between the changes which take place on substitution in the absorption of amides and the above ureas,<sup>15</sup> the explanation probably lying in the possession of a zwitterion constitution by urea, to which there is no corresponding constitution in substituted amides.

(c) The Absorption of Iso-Ureas.\*—According to Hantzsch,<sup>10</sup> on account of the similarity in their absorption spectra the constitutions

\* Measured in this laboratory by Gavin D. Pearson.

of benzamide and its ethyl derivative will be represented by (I) and (II) respectively. Two analogous urea derivatives have been measured, O-methyl-*iso*-urea and O-ethyl-*iso*-urea hydrochloride, the hydrochloride being



measured in the second instance on account of the instability of the free O-ethyl-*iso*-urea, their absorption spectra being given in Fig. 4, where it will be seen that both the free base and the hydrochloride have

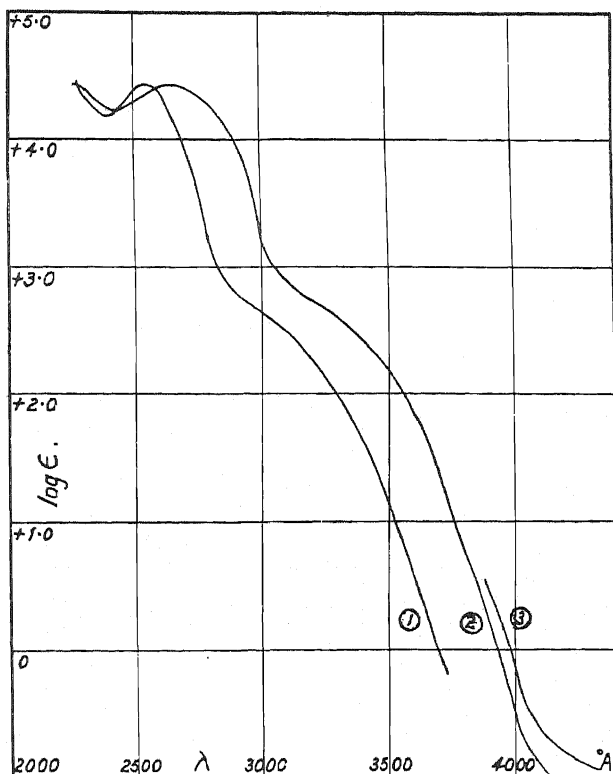
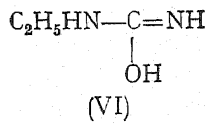
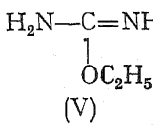
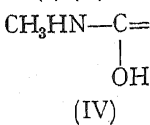
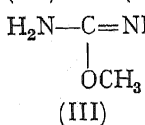


FIG. 6.—(1)  $\text{N,N,N',N'-tetraethylthiourea}$  in alcohol.  
(2)  $\text{N,N,N',N'-tetraethylthiourea}$  in alcohol.  
(3)  $\text{N,N,N',N'-tetraethylthiourea}$  as pure liquid.

practically the same absorption. It is now possible to compare (a) (III) with (IV) and (b) (V) with (VI).



As the N-substituted ureas were represented as having a constitution lying between that of a zwitterion and an amino-imino structure it was thought probable that there would be a similarity in the absorption of the normal and *iso*-ureas, but it is evident from the curves just given that the effect of substitution outweighs any other effects that might be present.



(d) **The Absorption of Phenyl-substituted Ureas.**—The substitution of phenyl groups in urea introduces certain new complications on account of the benzene ring itself possessing an absorption characterised by a number of fine bands. These bands disappear in certain compounds, *e.g.*, diphenyl, and in none of the phenyl substituted ureas investigated has any evidence of them been found. The absorption of the phenyl group would be expected to make a considerable difference between the absorption spectra of alkyl and aryl ureas even if the constitution of the molecules remained identical, a surmise which is borne

out by experiment. The absorption curves of five phenyl substituted ureas are given in Fig. 5, which reveals immediately the profound influence which the phenyl group has on the absorption, making it quite impossible to compare these ureas with those which have already been discussed.

Three of the curves, those for N . N'-dimethyl-N . N'-diphenyl-urea, N . N'-diethyl-N . N'-diphenyl-urea and N . N-diphenyl-urea, make an identity of structure almost certain. The two tetra-substituted ureas must be true carbamides, so this suggests that N . N-diphenyl-urea is also a true carbamide in agreement with its diamagnetic susceptibility. Between these three absorption spectra and those of N-phenyl-urea and N . N'-diphenyl-urea there is a considerable difference. From the diamagnetic susceptibility it was believed that N-phenyl-urea had a constitution represented by (VII), which is not inconsistent with its

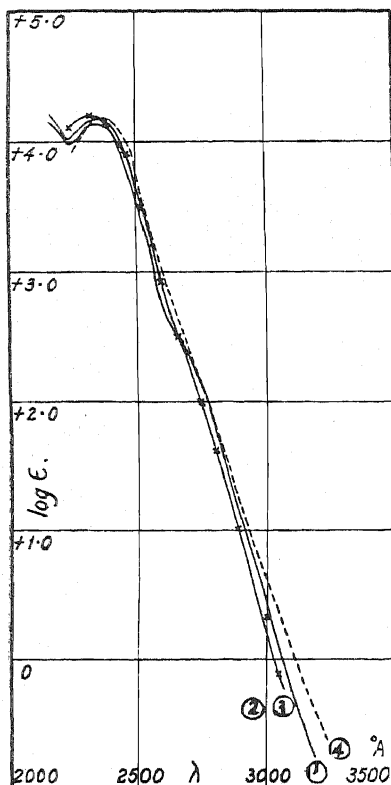
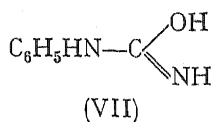


FIG. 7.—(1) Thiourea.  
(2) N-methyl-thiourea. x—x  
(3) N-ethyl-thiourea.  
(4) N-allyl-thiourea.  
in water.



having an absorption spectrum different from that of the completely substituted ureas. Similarly, there is a difference magnetically between the N . N and N . N'-diphenyl-ureas, which was interpreted as arising from the N . N'-diphenyl-urea having an amino-imino structure. Although N-phenyl-urea and N . N'-diphenyl-urea have not identical absorption spectra, this is not inconsistent with the above suggestions regarding their constitutions as the presence of the second phenyl group might be the cause. Further evidence is the difference between the absorptions of N . N'-diphenyl-urea and N . N'-dimethyl-N . N'-di-

phenyl-urea, which differ by more than can readily be accounted for by the substitution of two methyl groups for two hydrogen atoms.

Reviewing the ultra-violet absorption of the urea molecule; urea itself is highly transparent, and this transparency is only slightly lessened by mono-substitution, provided always that the substituent is not chromophoric. There is a considerable increase in absorption on complete substitution, but in no case investigated is selective absorption exhibited. N. N-dimethyl-urea alone has an absorption curve which might be differentiated from those of the other ureas, probably attributable to the same difference in constitution which was revealed by its diamagnetic susceptibility. When the substituents are phenyl groups the whole absorption curve is dominated by their presence, but nevertheless smaller changes in the absorption spectra which are still present can be referred to constitutional changes within the molecule. While the absorption spectra of the phenyl ureas bear a considerable resemblance to those of the aryl amides,<sup>13, 15</sup> difficulties in the determination of the constitutions of the latter compounds make it unsound to draw dogmatic conclusions based on the similarity of the absorption curves of the two series of derivatives.

## Part II.—Thioureas.

Although in general little is known of the ultra-violet absorption of thio compounds, the difference between the absorptive powers of the  $-S-H$  and  $-O-H$ ,  $=C=S$  and  $=C=O$  groups would be expected to make a considerable difference between the absorptive powers of ureas and thioureas. Furthermore, the magnetic investigation of these compounds showed that there is less variation in the constitution of the thiourea molecule on substitution than in urea, the former molecule not giving a zwitterion as did urea, thus one would expect less variation in the absorption spectra of thioureas than in ureas.

(a) **The Absorption of True Thio-Carbamides.**—As before it will be advantageous to consider the absorption of the tetra-substituted thioureas first, and in Fig. 6 will be found the absorption curves of N. N—N', N'-tetramethyl-thiourea and N. N—N', N'-tetraethyl-thiourea, the latter as a pure liquid, over a short range of wave-lengths as well as in solution, which as in the other urea derivatives examined has

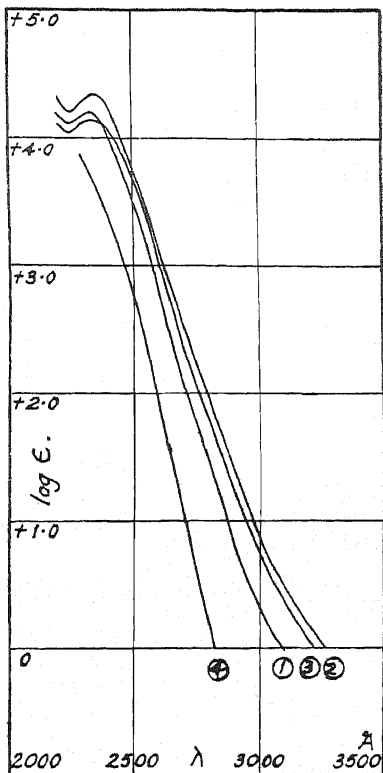


FIG. 8.—(1) N. N'-dimethyl-thiourea.  
(2) N. N'-diethyl-thiourea.  
(3) N. N-dimethyl-thiourea.  
(4) O-methyl-iso-thiourea.  
hydrochloride in water.

sensibly the same absorption whether as pure liquid or in solution. These absorption spectra are distinct from those of tetra-substituted urea derivatives. Both compounds have practically the same absorption spectrum which gives indications of consisting of three bands, the third of which does not attain its maximum within the range investigated. It is doubtful if one can assign any of these bands to specific parts of the molecules, as very diverse thio-compounds have absorption spectra of a similar type.<sup>5</sup>

**(b) The Absorption of Incompletely Substituted Thioureas.—**

As already mentioned, there is no magnetic evidence for the existence of thiourea as a zwitterion, which reduces the possible changes in constitution which may take place on substitution. From the value of its diamagnetic susceptibility thiourea appears to be an amino-imino resonance hybrid which changes towards a true thio-carbamide on substitution. Thus there are only two possible constitutions for substituted thioureas, compared with three in the case of urea, in

consequence of which less varied absorption spectra are to be expected. Figs. 7 and 8 give the absorption curves of thiourea, N-methyl-, N-ethyl-, N-allyl-, N.N- and N.N'-dimethyl-, and N.N'-diethyl-thiourea, all of which have practically the same absorption curves, with an absorption maximum between 2300 and 2400 Å. and an extinction coefficient whose logarithm is about 4.

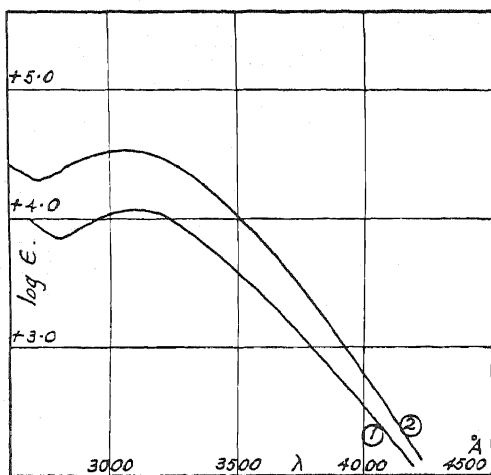


FIG. 9.—(1) N.N'-diphenyl-N'-acetyl-thiourea.  
(2) N.N-N'.N'-tetraphenyl-thiourea,  
in alcohol.

The diamagnetic susceptibilities of the substituted compounds suggested a constitution made up of both the

amino-imino and true carbamide forms, and the pronounced similarity in their absorption spectra is in agreement with their all having the same constitution, which would be nearer that of the unsubstituted thiourea than in the case of urea and its derivatives.

While di-substituted thioureas have different diamagnetic susceptibilities for the N.N- and N.N'-isomers indicating a difference in constitution, the difference being in favour of a greater preponderance of thio-carbamide in the N.N-derivatives, the absorption spectra of N.N-dimethyl- and N.N'-dimethyl-thiourea have only fractionally different absorption coefficients, the shape of the absorption curves being practically identical.

**(c) The Absorption of Phenyl-Thioureas.—**The introduction of phenyl groups into the urea molecule caused a very marked change in the nature of the absorption curve; the same introduction into thiourea, however, does not make such a marked change owing to the fact that the absorption curve of thiourea itself is not unlike the selective ab-

sorption curve of the phenyl group. One *o*-tolyl- and eight phenyl-substituted thioureas have been investigated, and as will be seen from Figs. 9 and 10 their absorption spectra fall into two groups, differing considerably in the width and position of the maximum of their absorption band. The first group contains N . N-diphenyl-N'-acetylthiourea and N . N—N' . N'-tetraphenylthiourea, the second N-phenyl-, N . N-diphenyl-, N . N'-diphenyl-, and N . N'-dimethyl-N . N'-diphenyl-, N . N-dimethyl-N'-phenyl-, N-phenyl-N'-ethylol-, N . N-dipropyl-N'-*o*-tolylthiourea.

The relative positions of the absorption bands in N . N—N' . N'-tetramethyl-thiourea, N . N' -dimethyl - N . N' -diphenyl-thiourea, and N . N—N' . N'-tetraphenylthiourea are qualitatively the same as those given by Rivier and Borel, who also obtained the very wide absorption band for N . N—N' . N'-tetraphenylthiourea.

The N . N—N' . N'-tetraphenyl-thiourea in the first group must undoubtedly be a true carbamide, but its absorption band cannot be attributed solely to a thio-carbamide constitution, this form of absorption band being caused rather by the presence of two phenyl groups attached to the same nitrogen atom combined with the impossibility of amino-imino group formation.

As N . N-diphenyl-N'-acetylthiourea displays the same type of absorption it probably also has a thio-carbamide constitution. Here we also have two phenyl groups attached to the same nitrogen atom, and one of the remaining hydrogen atoms replaced by an acetyl group, so it would appear that the conditions for this type of absorption are firstly the weighting of one end of the thiourea molecule with two groups such as phenyl groups, a methyl or single phenyl group not being sufficient, combined with some deterrent to the formation of an amino-imino structure. This suggestion is strengthened by the further examination of the absorption curves of the thioureas given in Fig. 10, which have their absorption maxima some 400 Å. further

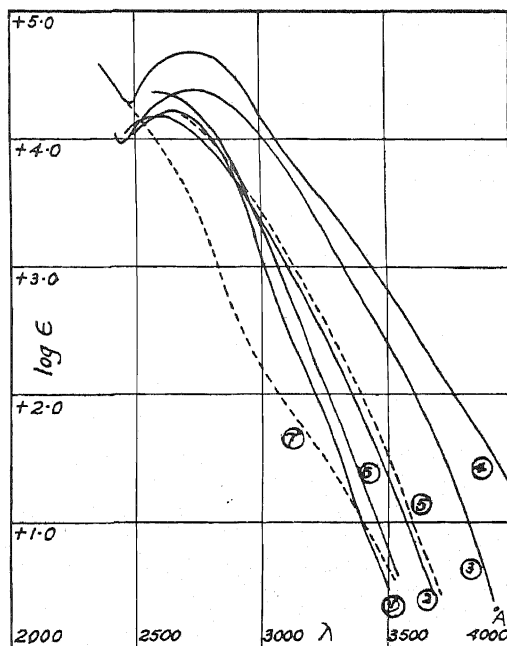


FIG. 10.—(1) N-phenyl-thiourea.  
(2) N . N-diphenyl-thiourea.  
(3) N . N'-diphenyl-thiourea.  
(4) N . N'-dimethyl-N . N'-diphenyl-thiourea.  
(5) N . N-dimethyl-N'-phenyl-thiourea.  
(6) N-phenyl-N'-ethylol-thiourea.  
(7) N . N-dipropyl-N'-*o*-tolyl-thiourea.  
in alcohol.

into the ultra-violet. Here N. N'-dimethyl-N. N'-diphenyl-thiourea has the broadest absorption band which is, however, still distinct from the two thioureas given in Fig. 9. As already suggested this type of absorption does not arise from the presence in the molecule of a  $=C=S$  group alone, but rather from the presence of two phenyl groups. From its diamagnetic susceptibility N-phenyl-thiourea was approaching a constitution represented by a pure thiocarbamide, while wholly thio-carbamide constitutions were suggested for N. N. and N. N'-diphenyl-thiourea. None of the phenyl-substituted thioureas have the same type of absorption curve as that characteristic of N. N. N'. N'-tetramethyl- and N. N. N'. N'-tetraethyl-thiourea, a difference which must be attributed to the influence of the phenyl group. As will be realised from the absorption curves of these urea derivatives the inter-relationships in this group are exceedingly complex, due to the reaction of the substituent chromophore on the chromophoric group of the parent molecule, and the effect of weighting one end of the molecule on the probability of its assuming an amino-imino constitution.

(d) **The Absorption of iso-Thioureas.**—The absorption of one *iso*-thiourea has been measured as its hydrochloride, *viz.*, *o*-methyl-*iso*-thiourea hydrochloride, the absorption curve being given in Fig. 4. It will be seen that it has the general form characteristic of the simpler thioureas, and that, barring its somewhat lower absorption coefficient, it is indistinguishable from its N-isomer.

### Summary.

The ultra-violet absorption of some thirty-five urea and thiourea derivatives has been measured, mostly for the first time, over the range 2200 Å. to 4000 Å., and their absorption curves correlated with their chemical constitution as determined from their diamagnetic susceptibilities.

The authors wish to express their gratitude to Professor A. J. Allmand, King's College, London, and Professor Alex. Findlay, Marischal College, Aberdeen, for their interest in this work, and to thank the Carnegie Trustees for a Teaching Fellowship. They also wish to acknowledge a gift of several substituted thioureas from Professor E. A. Werner, Trinity College, Dublin.

*King's College,  
London University.*

*Marischal College,  
Aberdeen University.*

# EXPERIMENTS ON INCREASING THE CHEMICAL ACTIVITY OF CADMIUM IODIDE BY IRRADIATION.

By J. ARVID HEDVALL, P. WALLGREN AND S. MÅNSSON.\*

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Much attention is nowadays given to the influence of structure or, generally, of lattice building factors on the physico-chemical properties of solids. Some of the most important results of investigations concerning these topochemical problems can be summed up as follows:

There are three kinds of lattice irregularities, which are all of importance for the chemical activity of a solid substance. Schottky and C. Wagner<sup>1</sup> have worked out the theory of the *reversible* lattice defects based on previous work carried out above all by Fajans,<sup>2</sup> Frenkel,<sup>3</sup> v. Hevesy,<sup>4</sup> Jost,<sup>5</sup> Smekal,<sup>6</sup> and Zwicky.<sup>7</sup> These defects are produced by the thermal vibrations of the lattice particles, and are due to interstitially placed particles of great mobility or to migrating lattice holes, from which such particles have been removed, or to the normal ions of the compounds having been substituted by ions of greater charge, or to stoichiometric anomalies. Thermodynamically considered, the reversible defects always correspond to equilibrium states of the crystals. In recent years Wagner and his co-workers have shown that the experimentally determined rate of diffusion processes accords well with that found by this theory. In a few systems, where the reversible defects are very pronounced, and are not influenced by other (irreversible) structural irregularities, it has also been possible to follow kinetically the course of chemical reactions between solids, e.g.  $2\text{AgI} + \text{HgI}_2 = \text{Ag}_2\text{HgI}_4$ .

In very many systems, however, where solid substances are characterised by a more or less pronounced chemical activity without possessing ionic conductivity the reaction capacity must be ascribed to other structural defects, generally known as *irreversible* or *topochemical* irregularities. These have been utilised, especially when preparing catalysts and adsorbents. Results obtained during the last twenty or thirty years have shown that it is just this kind of structural influence which is of profound importance in determining the real reaction capacity and surface activity of solids generally.<sup>8</sup> We now know that such

\* Owing to the interruption of Scandinavian mails the authors have been unable as yet to correct proofs of this paper. The Editor is much indebted to Prof. J. D. Bernal for looking through the proof.

<sup>1</sup> C. Wagner and W. Schottky, *Z. physikal. Chem. B*, 1930, **11**, 163; W. Schottky, *Z. Elektrochem.*, 1939, **45**, 33; C. Wagner, *Ber., Deutsch. Keram. Ges.*, 1938, **19**, 207.

<sup>2</sup> K. Fajans, *Z. Krist.*, 1925, **61**, 39; 1928, **66**, 321.

<sup>3</sup> J. Frenkel, *Z. Physik*, 1926, **35**, 652.

<sup>4</sup> G. v. Hevesy, Geiger and Scheel, *Handbuch Physik*, **13**, 286.

<sup>5</sup> W. Jost, *J. Chemical Physics*, 1933, **1**, 466; *Z. physik. Chem. B*, 1936, **32**, 1; *Diffusion und chemische Reaktion in festen Stoffen* (Dresden, 1937).

<sup>6</sup> A. Smekal, Geiger and Scheel, *Handbuch Physik*, **24**: 2, 795-922.

<sup>7</sup> F. Zwicky, *Proc. Nat. Acad. Sci. U.S.A.*, 1929, **15**, 524; *Physic. Rev.*, 1931, **38**, 1772.

<sup>8</sup> J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938); *Chemic. Rev.*, 1934, **15**, 139.

irregularities, which do not correspond to equilibrium states, and consequently represent an excess of lattice energy,<sup>9</sup> may be due to an incomplete development of the lattice of the reaction product, formed from substances (or crystallographic modifications of other composition or symmetry) which have been incompletely eliminated (inheritance factors<sup>10</sup>), or due to "frozen" reversible structures, corresponding to higher temperatures. Such states of faulty structure can be produced by quenching substances down to temperatures at which the lattice is too rigid to allow the particles to diffuse into their normal positions. This kind of activity consequently disappears when the rigidity of the lattice in question begins to relax. If the time of heating is adapted to the rate of the structural change, it is often possible to show that the reaction intensity of a substance, the activity of which depends on such lattice anomalies, has a relative maximum at transition temperatures of different kinds.<sup>11</sup>

Since the systematic study of the reaction properties of solids began, about twenty-five years ago, many reactions have been described, which occur in systems of non-conductors, or at such low temperatures that it is impossible to explain the chemical interchange by migrating ions. For example:  $\text{BaO} + \text{CaSO}_4 = \text{BaSO}_4 + \text{CaO}$  (about  $370^\circ \text{C.}$ );  $\text{CaO} + \text{CuSO}_4 = \text{CaSO}_4 + \text{CuO}$  (about  $515^\circ \text{C.}$ );<sup>12</sup>  $\text{BaO} + \text{CoO} \cdot \text{Al}_2\text{O}_3 = \text{BaO} \cdot \text{Al}_2\text{O}_3 + \text{CoO}$  (about  $350^\circ \text{C.}$ );<sup>13</sup>  $\text{CaO}, \text{SrO} + \text{Ag}_2\text{SO}_4 = \text{Ca}, \text{SrSO}_4 + 2\text{Ag} + \text{O}$  (about  $415^\circ \text{C.}$ ; transition point of  $\text{Ag}_2\text{SO}_4$ :  $411^\circ \text{C.}$ );<sup>14</sup> and other similar reactions taking place at a transition point of one of the components,<sup>15</sup> e.g. the formation of solid solutions or silicates in powder mixtures containing quartz at its transition points ( $575^\circ \text{C.}$ ,  $\alpha \rightleftharpoons \beta$ ; about  $870^\circ \text{C.}$   $\alpha$ -quartz-cristobalite).<sup>16</sup> Such systems undoubtedly show that a transport of reacting matter in solid state can also be carried out by other particles than ions.<sup>17</sup>

This can be understood, if we remember that not only the mobility, but also the character of the particles at inner or outer surfaces, or in incomplete reaction films, differ very much from the conditions of the normal interior lattice. No doubt several phenomena of this kind are closely related, on the one hand, to the change of position of those atom complexes of anhydride type the formation of which must precede the thermal breakdown of the lattices of salts of oxygen acids, and, on the other, to the chemical activity of such dipoles of molecular type as are observed in adsorption films on metals.<sup>18</sup>

In fact, however, it is impossible to find a general explanation of the mechanism of reactions of solids. Indeed, the conditions may vary widely, not only from one system to another, but also for the formation of the same reaction product in different temperature intervals. In addition, consideration must also be given to the topochemical influence of different modes of preparing the reacting substances and of the reaction conditions in general.

A third group of lattice changes can influence the physico-chemical activity. We are not limited merely to a thermal influence on the lattice. As was shown some years ago, there is also a connection between the

<sup>9</sup> R. Fricke, *Z. Elektrochem.*, 1934, 40, 630; 1939, 45, 254.

<sup>10</sup> G. Hüttig, *Sitz.Ber. Akad. Wiss. Wien*, 1936, 7, 648.

<sup>11</sup> J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), p. 141.

<sup>12</sup> *Ibid.*, p. 68.

<sup>13</sup> *Ibid.*, p. 197.

<sup>14</sup> *Ibid.*, p. 73.

<sup>15</sup> *Ibid.*, pp. 127-42.

<sup>16</sup> *Ibid.*, p. 212.

<sup>17</sup> *Ibid.*, p. 132.

<sup>18</sup> *Ibid.*, pp. 69-72; J. H. de Boer and E. J. E. Verwey, *Rec. trav. chim. Pays Bas*, 1936, 443, 675.

magnetic or electric properties of a substance and its chemical activity. In very many combinations of catalysts and substrate reactions we have found an abrupt change in the catalytic effect of ferromagnetic substances when passing through their Curie-intervals.<sup>19</sup> Investigations still going on show that the activation energy of the paramagnetic state above the Curie-point is greater than for the ferromagnetic lattice.<sup>20</sup> Now the catalytic effect is, without exception, greater above the Curie-point, and this can only be understood if we assume that the corresponding disorder of the elemental magnets makes it possible for the greater part of the surface to act as catalysing centres.

The electrical analogy to this *magneto-catalytic effect* has also been found. Many organic substances undergo at fixed temperatures a displacement of the electric fields of their molecules, without change of crystallographic structure, quite in conformity with the change in magnetic properties mentioned. It might be expected that changes of this type would also influence the chemical activity of the substance in question. Experiments carried out with pastilles of *Rochelle salt* have shown that the rate of solution is abruptly changed<sup>21</sup> at 22° C. Above this temperature the polar forces of the OH-radicals seem to cause a strengthening of the lattice, and consequently a smaller chemical activity of the surface,<sup>22</sup> or at least of special crystal faces.

Recent investigations have shown that the irradiation of solids can produce effects other than those generally described as photochemical activation, *i.e.* in the form of real chemical changes in the substance or in an adsorption film by means of excited electrons.

Hedvall and co-workers have found that it is also possible to influence the chemical activity of the surface itself by means of absorbable radiation. Effects of this kind must be due to the fact that the excitation of lattice particles, by removal of electrons to higher levels, changes the binding forces of the lattice and, thus, also the activity of the surface. Accordingly, adsorption equilibria between solids and dissolved substances can be changed by irradiation.<sup>23</sup> The action of light may bring about either an increase or a decrease in the quantity adsorbed per surface unit in comparison with the adsorption in darkness.<sup>24</sup>

### Irradiation Experiments with Cadmium Iodide.\*

The above-mentioned experiences suggested that substances with fibrous or layer lattices would have different photosensitivity on different surfaces. It might be presumed that the surfaces parallel to the layers, being closely packed with particles bound together by strong forces, would be more stable towards this kind of action than the prism planes sparsely set with more loosely bound atoms or ions.

As typical compounds of this kind we chose CdI<sub>2</sub>, which we have used either (a) as pastilles of laminæ (surface about 2-3 mm.<sup>2</sup>), parallel to each other, so that the bounding surface of the cylinder is formed of the thin prism planes, or (b) as larger single crystals (basis planes about 6-7

<sup>19</sup> J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 162-170.

<sup>20</sup> G. Cohn (as yet unpublished).

<sup>21</sup> J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 171-4.

<sup>22</sup> J. A. Hedvall, *Atti X. Congr. internat. Chimica Roma*, 1938, II, pp. 255, 268 (discuss. Wulff).

<sup>23</sup> J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 175-85.

<sup>24</sup> J. A. Hedvall, G. Cohn, A. Assarsson and S. Berger, *Nature*, 1939, 143, 330.

\* Together with P. Wallgren.



mm.<sup>2</sup>, height of prism faces about 1.2 mm.). The preparations were carefully purified and dried and then kept in vacuum desiccators.

The lattice of CdI<sub>2</sub> is built up as shown in (A), in chains or layers. I- It crystallises in the type <sup>25</sup> C : 6, with a distance of 3 Å. between Cd++ the Cd- and I-ions and 4.21 Å. between the layers (I- — I-).<sup>26</sup>

I- During irradiation by a quartz-Hg-lamp the crystals or pastilles (A) were kept in a quartz tube, where if required they could be rotated.

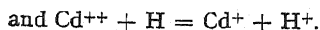
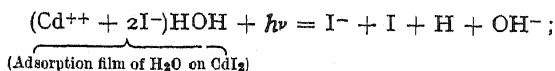
The temperature was kept constant at 20° C. during irradiation, and the distance between the quartz tube and the lamp was 15 cm. So that the experiments could be carried out in different atmospheres, a gas current of constant speed (30 c.c./min.) could be passed through the tube. Purifying and drying bottles and U-tubes with P<sub>2</sub>O<sub>5</sub> or bottles with H<sub>2</sub>O, kept at the proper temperature by means of a thermostat, were used to keep the gas in question dry, or, if desired, at a definite moisture content.

It was found, in perfect accordance with our presumption, that pastilles or single crystals, without exception, became dark coloured only at the prism faces, when irradiated in atmospheres or air, N<sub>2</sub> or H<sub>2</sub> of normal humidity. This effect was observable after only one or two minutes. The basis planes of the cylindrical pastilles, being composed of a number of crystals, became blackened only at the limits between the different laminae, producing a pattern as by etching (Fig. 1, Plate X.).

No effect could be observed when irradiating by wave-lengths which are not absorbed by CdI<sub>2</sub>, even though the irradiation was continued for two hours. Consequently the removal of all visible light by a black filter was of no influence and no action was observed on irradiation by X-rays (Cu anti-cathode). Previous work on the photo-chemical stability of many compounds, *e.g.* Cu-<sup>27</sup> and Ag-halides<sup>28</sup> and sulphides<sup>29</sup> has shown that the presence of water vapour is a necessary condition for the chemical decomposition by light and that even traces of H<sub>2</sub>O greatly increase the rate of reaction. We, also, have found in a series of experiments carried out in carefully dried gases that, without exception, there was no visible action on the preparations; all surfaces were unchanged, even after very long exposures.

In other experiments under the same conditions, mixtures of dry N<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH vapour were passed over crystals of CdI<sub>2</sub>; visible action of light takes place only if the vapour is not carefully dried. As expected, the reaction always starts at edges, damaged points and scratches.

Accordingly, the photochemical action of ultraviolet light on the prism faces of CdI<sub>2</sub> seems to require the presence of at least small quantities of water. As usual, the photochemical process, which is observed as a dark colouring of the surfaces, is not easy to describe exactly. However, it seems reasonable to presume that the mechanism may be similar to that which Weiss<sup>30</sup> considers probable, when ZnS is irradiated under circumstances similar to those in our experiments:



It is, of course, possible that, under suitable conditions, the decomposition of CdI<sub>2</sub> may proceed further, resulting in the formation of molecular I<sub>2</sub>, H<sub>2</sub> and metallic Cd. Although the experimental conditions should

<sup>25</sup> Z. Krist., Erg.-Bd. II (1928-32), p. 247.

<sup>26</sup> *Ibid.*, I (1913-28), p. 189.

<sup>27</sup> J. Plotnikow, *Allgem. Photochem.* (Berlin, 1936), p. 430.

<sup>28</sup> J. Plotnikow, *ibid.*, pp. 446, 451-5.

<sup>29</sup> C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 902.

<sup>30</sup> J. Weiss, *ibid.*, 1938, 34, 909.

favour a complete decomposition of  $\text{CdI}_2$ , we were never able to find even traces of the free elements in question. These experiments were carried out as follows: Fine powders of  $\text{CdI}_2$  were kept in rotation and irradiated for 5 hours in currents of moist  $\text{N}_2$ ,  $\text{H}_2$ , or  $\text{C}_2\text{H}_4$  at temperatures between  $20^\circ$  and  $50^\circ \text{C}$ ., the gases being afterwards absorbed in small quantities of suitable solvents. After long irradiations the inside wall of that part of the quartz tube in which the powder was kept in rotation became a little dark. No traces of free  $\text{I}_2$  or  $\text{Cd}$  were, however, found, and on treating this dark film with an acid no evolution of  $\text{H}_2$  was observed. Water or solutions containing water made the coloration vanish, as was the case if the irradiated crystals were so treated, or if they were kept in a moist atmosphere after the irradiation. When shaking the irradiated powder with an organic solvent, also, no free iodine was found.

These experiences suggest that the photochemical process in  $\text{CdI}_2$  can stop at that stage, at which there is an oscillation in the  $\text{CdI}_2$  chains between the states (A), (B) and (C), involving a weakening of the binding forces or a loosening of the lattice. No difference was observed between pastilles or crystals prepared as described above and those which had been heated for 3 days at  $150^\circ \text{C}$ . This had to be examined because of the possibility of the existence of two modifications of  $\text{CdI}_2$ .<sup>31</sup> Investigations carried out by G. and B. Aminoff, as yet unpublished, seem to show that only one modification exists, and that the observed structure variations can be explained by displacements of parts of the lattice layers.<sup>32</sup>

In order that such photochemical action can take place, it is evidently necessary, on the one hand, that valency electrons which are easily removable from their normal levels should be present, and, on the other, that an adsorption film of water, in which the deformation of the water molecules facilitates their dissociation in ions, should be formed.

Regarding the first condition, Werner<sup>33</sup> has established that  $\text{CdI}_2$  is a photoelectric conductor, and consequently possesses electrons easily liberated through absorption of radiating energy. As to the formation of a polarised adsorption film of  $\text{H}_2\text{O}$  favourable conditions for such a film evidently exist at the prism faces owing to their unsaturated adsorption forces.

Other observations seem to agree very well with our presumption that crystal faces intersecting lattice layers should possess special adsorption activity. Thus, Hofmann<sup>34</sup> has found a greater adsorption activity of the prism than of the basal faces of graphite, and Wolf and Riehl,<sup>35</sup> when keeping graphite crystals in air containing radioactive emanation, observed that the radiation was mostly emitted from these surfaces or from edges or crystal faults.

### Poisoning of the Surfaces against Water Adsorption.

It being proved that the photochemical effect is due to an interaction between loosely bound electrons and a highly activated adsorption film of  $\text{H}_2\text{O}$  and that the combination of these conditions, *i.e.* their accommodation to each other so that an action of light is produced, only takes

<sup>31</sup> Z. Krist., Erg.-Bd. III (1933-35), pp. 22, 282.

<sup>32</sup> Communication by Professor G. Aminoff (unpublished as yet).

<sup>33</sup> J. Werner, Z. Physik., 1929, 57, 219; cf. also E. Oeser, *ibid.*, 1935, 95, 699,

715.

<sup>34</sup> U. Hofmann, Z. angew. Chem., 1931, 41, 845.

<sup>35</sup> P. U. Wolf and N. Riehl, *ibid.*, 1932, 45, 400.

place at the prism faces, it was of interest to examine whether the effect would fail to appear if the crystals were first treated with substances which are more intensely adsorbed than water.

The choice of poisoning substances was made from the same viewpoint as in flotation technique, *i.e.* the compounds in question should possess high adsorption intensity to  $\text{CdI}_2$  and no affinity to water. The experiments were so carried out that vapours of oleic acid, stearic acid, thioglycollic acid, allyl mustard oil, benzene, toluene, phenol, aniline, *o*-toluidine, 1 : 3 : 4-xylydine and pyridine were passed over the crystals for 10 minutes at the lowest temperatures possible by means of an air current. During this treatment the crystals were, of course, not irradiated.

These substances can be divided into four groups, *viz.*, the pure fatty acids (known as water repellers but probably without strong adsorption forces to  $\text{CdI}_2$ ); the two aliphatic compounds, containing S-atoms, which might be assumed to increase the adsorption affinity to  $\text{CdI}_2$ ; benzene, toluene and phenol, which could not be expected to exert great influence, and, lastly, the cyclic compounds, containing  $\text{NH}_2$ - or N-radicals, where a more effective poisoning effect might be expected, owing to the disposition of  $\text{CdI}_2$  to give stable complexes with substances of this kind.

On subsequent irradiation under the same conditions as before (moist  $\text{N}_2$ ), except that two crystals or pastilles—the one being unpoisoned—were always irradiated together in order to facilitate comparison of the observations, the following results were obtained. As expected, *phenol* had no influence, the adsorption film evidently being easily replaced by water. *Benzene* and *toluene*, also, had no influence. The treatment with *fatty acids*, however, showed a distinct effect; the dark colouring of the untreated crystals was, as usual, readily observable within a minute, whereas the poisoned ones remained white much longer. Even after irradiation for 15 minutes or more there was a great difference in colour between the two crystals. The gradual blackening also of the poisoned crystals is probably due to destruction of the poison film by the ultraviolet light. *Thioglycollic acid* exerts about the same effect as the unsubstituted fatty acids. *Allyl mustard oil* is more effective, preventing visible attack of the light for about 10-15 minutes, depending on the duration of the poisoning treatment. Still greater effect is, as expected, obtained with crystals, treated with *aniline* and 1 : 3 : 4-*xylydine*, and especially with *o*-*toluidine*, which still prevents the action of light after two hours, thus having practically completely poisoned the surface.

As mentioned above, it is not sufficient for an effective poison that one part of the molecule is intensely adsorbed. The part facing outward from the crystal surface must not have great affinity to water. Therefore experiments with crystals treated with dry  $\text{NH}_3$  showed no poisoning effect at all. The surfaces were, however, not so uniformly attacked as before, because of the formation of a complex between  $\text{CdI}_2$  and  $\text{NH}_3$ , starting at scratches, edges, or damaged points of the surface.

*Pyridine* proved, however, to be the most effective poison of all substances tested. Treated with vapour of pyridine and dried in vacuum desiccators the crystals remained white when subsequently irradiated in moist  $\text{N}_2$  for hours.

The difference in poisoning effectiveness between aniline, xylydine, *o*-toluidine and pyridine corresponds very well with the differences in the chemical behaviour of  $\text{CdI}_2$  towards these substances, with all of which it forms addition products, the intensity of the reactions increasing from aniline to pyridine.

The reaction with pyridine deserves somewhat more detailed description. When used in great excess, the crystals absorb it intensely, developing a considerable reaction heat and swelling like graphite when oxidised to graphite acid. The reaction product remains solid if the proportion  $\text{C}_5\text{H}_5\text{N} : \text{CdI}_2$  does not exceed about 35 : 1. When kept in a vacuum

desiccator the crystals lose the larger part of the pyridine until an equilibrium is attained corresponding to the formula:  $\text{CdI}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ . This compound is insoluble in water.

It is of interest to mention that  $\text{CdBr}_2$  and  $\text{CdCl}_2$  behave in a similar way to  $\text{CdI}_2$  towards aniline, xylidine, *o*-toluidine and pyridine.  $\text{CdF}_2$ , however, behaves differently.

### Irradiation Experiments with $\text{CdBr}_2$ , $\text{CdCl}_2$ and $\text{CdF}_2$ .

Having shown that the photochemical reaction in  $\text{CdI}_2$  is made possible through combination of structural and adsorption factors, it was of interest to examine also the other Cd halides from this point of view. Experiments with them were carried out in exactly the same way.

$\text{CdBr}_2$  and  $\text{CdCl}_2$  were crystallised from solutions in water and dried in exactly the same way as when preparing  $\text{CdI}_2$ . The  $\text{CdF}_2$  used was "*Kahlbaum pro analysi*."

$\text{CdBr}_2$  crystallises<sup>36</sup> in the type *C*: 19.

$\text{Br}^-$

The  $\text{Cd}^{++}$  chains (*B*) form layers similar to those in  $\text{CdI}_2$  crystals.

$\text{Br}^-$

(*D*)

The only difference between the  $\text{CdI}_2$ - (*C*: 6) and  $\text{CdBr}_2$ -structures consists in the correlation of the anions, which in *C*: 6 form a hexagonal, and in *C*: 19 a cubic packing,<sup>37</sup> and in the smaller distances between the layers, both of which are caused by differences in volume and polarisation effects of the anions. Exactly as was the case with  $\text{CdI}_2$ , another "modification" exists, evidently formed when pressing or grinding crystals, and brought about by a periodical displacement of parts of the lattice.<sup>38</sup> This structure represents a kind of intermediate structure between  $\text{CdI}_2$  (*C*: 6) and  $\text{CdBr}_2$ . It can be transformed into the normal one (*C*: 19) by heating to about 200° C.

$\text{CdCl}_2$  also belongs to type *C*: 19, and the lattice data conform with those of  $\text{CdBr}_2$ , except for the different distance between adjacent layers.

Finally,  $\text{CdF}_2$  belongs to another class of symmetry, the fluorite type<sup>39</sup> *C*: 1, and it can, therefore, be presumed that the behaviour of  $\text{CdF}_2$  will differ fundamentally from the other compounds.

On irradiating these compounds in moist  $\text{N}_2$ , it was only that  $\text{CdBr}_2$  modification which is related to  $\text{CdI}_2$  (and produced through stressing the crystals) which was coloured dark after an exposure of some minutes. Irradiation in an atmosphere of dry  $\text{N}_2$  had no effect. After heating the  $\text{CdBr}_2$  for an hour at 200° C., and so bringing it back to its normal type (similar to  $\text{CdCl}_2$ , *C*: 19) no action of light could be observed under the experimental conditions. Similarly, no effect was obtained with  $\text{CdCl}_2$ , nor, of course, with  $\text{CdF}_2$ .

Obviously it is impossible to claim that no photochemical action takes place, merely because no colour change is observed. It may be that a disturbance also occurs in the layer lattices of the normal modifications of  $\text{CdBr}_2$  and of  $\text{CdCl}_2$ , without giving rise to a dark colouring.

<sup>36</sup> Z. Krist., Erg.-Bd. II (1928-32), pp. 246-7.

<sup>37</sup> *Ibid.*, I (1913-28), pp. 742-3.

<sup>38</sup> *Ibid.*, I (1913-28), p. 188.

<sup>39</sup> *Ibid.*, II (1928-32), p. 280.

The facts, however, that (i) a visible effect is obtained with  $\text{CdI}_2$ , and, though not so strongly, with that modification of  $\text{CdBr}_2$  which is regarded as a combination of  $C:6$  and  $C:19$ , (ii) there is markedly less adsorption intensity at the prism faces of the stable  $\text{CdBr}_2$  and  $\text{CdCl}_2$  modifications than at those of  $\text{CdI}_2$ , which also makes weaker polarisation of the adsorbed water molecules probable, and (iii) that the photoelectric conductivities of  $\text{CdBr}_2$  and  $\text{CdCl}_2$ <sup>40</sup> are smaller, seem to indicate that the combination of conditions for photochemical action is especially favourable in  $\text{CdI}_2$ . A difference between  $\text{CdI}_2$  and the other Cd halides can also be predicted, because of the greater polarisation effect caused by  $\text{Cd}^{++}$  on the  $\text{I}^-$ , which is more sensitive than  $\text{Br}^-$  and  $\text{Cl}^-$  (Fajans). This dissimilarity corresponds to the differences in structure mentioned above.

### Experiments on the Solubility of Irradiated $\text{CdI}_2$ -Crystals.\*

It is to be expected that crystals, the surfaces of which are activated through irradiation, will become more intensely attacked by a reactive

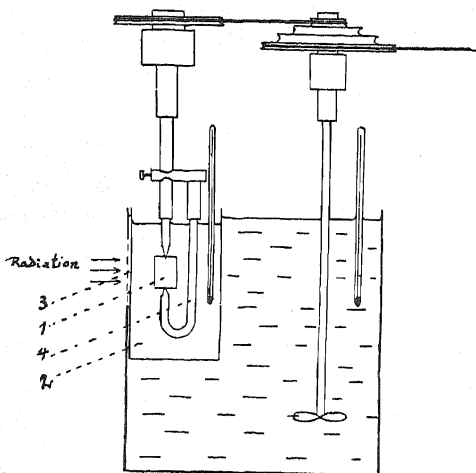


FIG. 2.

substance than when they have not been irradiated by absorbable wave-lengths. We therefore investigated the rate of solution of  $\text{CdI}_2$  pastilles, pressed in the way described above. As it was impossible to prepare two pastilles (the one to be irradiated, the other to be protected against the radiation) so perfectly equal as to permit a comparison of their rates of solution, the experiments were carried out with the same pastille. It was, of course, necessary to use a solvent which dissolves only a very small quantity of  $\text{CdI}_2$ , and which does not absorb the wave-lengths which exert the photochemical action on the crystal surface. These conditions are satisfied by a mixture of 92 parts by volume of "normal benzine" (freed from unsaturated hydrocarbons by treatment with  $\text{H}_2\text{SO}_4$ ), and 8 parts of alcohol (99.5 %  $\text{C}_2\text{H}_5\text{OH} + 0.5\text{H}_2\text{O}$ ). The solution experiments were carried out in a thermostat, the pastille (1) being rotated in a quartz tube (2) containing the solvent (75 c.c.) and placed close to a quartz window (3) on one side of the thermostat (Fig. 2). The pastille is supported by small springy glass bars (4), the upper and lower surfaces being covered by a wax which is not attacked by the solvent. The shortest wave-length emitted from the quartz-Hg lamp was 2350 Å. The solvent transmits light of wave-lengths longer than 2130 Å. and  $\text{CdI}_2$  absorbs wave-lengths shorter<sup>41</sup> than 3700 Å. The distance between the lamp (which had a quartz condenser lens) and the pastil was 3-4 cm., and the temperature was kept

<sup>40</sup> G. A. Dina, *Compt. rend.*, 1913, 157, 590, 736.

\* Together with S. Månsson.

<sup>41</sup> K. Butkow, *Acta physicochim. U.R.S.S.*, 1935, 3, 205.

constant at 25° C. during an experiment of 30 minutes. Every pastille was placed in a special desiccator communicating with a vacuum pump after the experiment. After 6 hours the solvent had evaporated and the pastils attained constant weight.

The table shows the results obtained under different conditions with pastils 1 to 5. It is seen that an increased rate of solution is produced by irradiation with wave-lengths which can be absorbed by  $\text{CdI}_2$ . An average effect of about 13 % is attained under the experimental conditions used.

The experiment thus proves that the presumption that surfaces which are photochemically sensitive can also, when irradiated, be activated with regard to their chemical behaviour in general.

**(A) Irradiation by Hg-Lamp without Black Filter.**

Pastil No.	Weight (in g.).	Quantity Dissolved (in g.).		Difference (in g.).	Effect of the Irradiation (%).
		In Darkness.	When Irradiated.		
1	6.690	0.00210	0.00235	0.00025	+ 11.9
2	8.034	0.00230	0.00254	0.00024	+ 10.5
3	7.194	0.00280	0.00328	0.00048	+ 17.0
1	6.687	0.00187	0.00217	0.00030	+ 16.0
2	8.029	0.00278	0.00310	0.00032	+ 11.5
4	7.854	0.00250	0.00290	0.00040	+ 16.0
				Average	+ 13.8

**(B) Irradiation by Hg-Lamp and a Black Filter, Transmitting no Visible Light.**

1	6.671	0.00250	0.00276	0.00026	+ 10.4
2	8.010	0.00300	0.00341	0.00041	+ 13.7
3	7.171	0.00258	0.00292	0.00034	+ 13.2
4	7.831	0.00237	0.00268	0.00031	+ 13.1
5	6.590	0.00355	0.00400	0.00045	+ 12.7
				Average	+ 12.6

**(C) Irradiation by White Light, containing no Ultraviolet Wave-lengths.**

1	6.672	0.00250	0.00240	- 0.00010
2	8.011	0.00258	0.00269	+ 0.00011
3	7.183	0.00260	0.00260	± 0.00000
4	7.840	0.00216	0.00207	- 0.00009
5	6.603	0.00259	0.00263	+ 0.00004
			Average	- 0.00001

**Summary.**

A short survey is given of the different kinds of faulty structure in crystal lattices, of the conditions for the production of irreversible irregularities or for the existence of the reversible ones in general, and of the importance of imperfectly formed crystals for different branches of chemistry. It is shown that increased chemical activity is caused not only by disturbance of crystallographic symmetry, but also by changes of the magnetic or the electric state of the lattice.

In accordance herewith photochemical effects have been found involving increased surface activity with respect also to the chemical interchange with surrounding materials. Arising from these experiments, the existence of crystals was assumed the photosensitivity of which may vary

with the kind of crystal faces. It was suggested that this might be the case with crystals built up as layer lattices. Experiments carried out with Cadmium halides have, indeed, shown that the prism faces of  $\text{CdI}_2$  are especially sensitive, whereas the basal faces are left unattacked by absorbable wave-lengths. The photochemical process requires small quantities of water adsorbed at the surface and, consequently, it can be more or less completely prevented by compounds which are more intensely adsorbed than water. A smaller effect of the same kind has been found when using that modification of  $\text{CdBr}_2$  which is of the same type (C : 6) as  $\text{CdI}_2$ . No visible action of radiation could be observed with  $\text{CdCl}_2$  and  $\text{CdF}_2$ , the lattices of which are more different from the type of  $\text{CdI}_2$ .

It has also been shown that the surface activity, caused by the photochemical process, involves increased rate of reaction of such parts of crystals; thus the prism faces of  $\text{CdI}_2$  when irradiated by absorbable wave-lengths, are more rapidly attacked by a solvent than in darkness, or if radiated by light not being absorbable.

The carrying out of this investigation has been made possible by subventions from the Nobel Committee for Chemistry of the Swedish Royal Academy of Science and the Research Fund of Chalmers Technical College.

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## REVIEWS OF BOOKS.

**The Mathematical Theory of Non-uniform Gases.** By S. CHAPMAN and T. G. COWLING. (Cambridge University Press, 1939, pp. 404. Price 30s.)

To those physicists who are primarily interested in phenomena, the dynamical theory of gases is an unsatisfactory subject. The fundamental principles are few, and can be readily applied to produce a crude theory, but, if we wish to obtain exact formulæ for the coefficients of viscosity, diffusion and thermal conductivity, long and complicated mathematical investigations are necessary. Further, these calculations add nothing to our understanding of the physical processes involved, though they are vitally necessary if we are to be able to deduce anything of value from the experimental material. It follows from the nature of the subject that books dealing with it should either be of an elementary nature or should be fully fledged mathematical treatises. Prof. Chapman and Dr. Cowling have chosen the latter alternative, and have presented the fullest account of the subject which has yet appeared in book form.

The book is a formidable one, even to a mathematical specialist, and the reading is not simplified by the authors' introduction of a new vector and tensor notation, too many of which already exist. Experimental physicists and physical chemists will probably find that the most useful part of the book consists of Chapters 12, 13 and 14, extending over 40 pages, where the various formulæ which have been deduced for different molecular models are compared in detail with the experimental results.

It is clear from even a casual glance at the book that a theory of such great mathematical complexity could not have evolved into such a state of perfection in a short time. The history of the subject is a long one, dating back effectively to Maxwell's paper of 1866, and an admirably written account is given in the historical summary at the end of the book. Although the dynamical equations had been set up at an early date by Maxwell and by Boltzmann, no general solution of them was given until 1916-17, when Chapman and Enskog published solutions independently. This work, and later improvements, forms the main topic of the book, and is now for the first time made widely available. In addition to discussions of the usual topics of viscosity, diffusion and thermal conductivity, treated by Enskog's method, there are also chapters on dense gases, ionised gases and the modifications introduced by the quantum theory. The small section dealing with the effect of the quantum theory on the molecular collisions is necessary to complete the account of the present state of the theory, but the incursion into the electron theory of metals could well have been dispensed with, since there the interest is mainly confined to the dynamics of the motion of the electrons in the crystal lattice, which is not dealt with in the book.

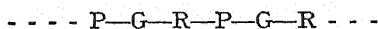
It is probable that the book will become the standard work of reference on the subject.

**The Molecular Structure of the Fibres of the Collagen Group. First Procter Memorial Lecture.** By W. T. ASTBURY. (London: International Society of Leather Trades' Chemists, 1940. Pp. 24. Price 2s. 6d.)

Dr. Astbury recently delivered the first Procter Memorial Lecture before the London Conference of the International Society of Leather Trades' Chemists. This has now been published in booklet form and thus made easily available to all workers interested in the problem of the structure of protein molecules or indeed of macro-molecules in general.

The lecture includes a first account of X-ray studies on collagen and elastin fibres carried out by Dr. Astbury and his colleague, Dr. Florence Bell.

The fibres of the collagen group are shown to have a special pattern of their own based on the arrangement of the amino acid residues in the long chain molecule, namely,



where P represents a proline or hydroxyproline residue, G, glycine and R, one or other of the remaining residues. Owing to the presence of the 5-atom ring in proline the stereochemical configuration of the chain differs from the more familiar pattern of the myosin-keratin group of fibres.

Collagen fibres show the property of "supercontraction" just like keratin fibres and there is a definite suggestion in the lecture that the fibrous form of protein molecules only exists as long as the long chain molecules are held extended by intra-molecular forces, and that the single molecule released from these external forces collapses into a looped or 3-dimensional form.



The lecture is written in Dr. Astbury's characteristically lucid style and the International Society of Leather Trades' Chemists have done a good service to chemistry in publishing it as a booklet.

D. J. L.

**Elementos de Atomística.** By Professor G. E. VILLAR. (Montevideo, Impresora Uruguaya, South America. 1939.

Professor Villar has put Spanish-speaking students in his debt by writing this very useful treatise on atomic physics. The treatment is strictly elementary throughout and the book may be read with profit by a university student in the pass grade. The topics usual to a first year course in this subject are covered, and the book can be recommended to English students of physics who desire to extend their knowledge of the Spanish language.

A. F.

**Sound.** By Dr. E. G. RICHARDSON. Pp. iv + 339. (London: Edward Arnold & Co., 1940. Price, 16s. net.)

Dr. Richardson's treatise, which now appears in its third edition, is too well known to need any detailed description here. The scope of the book remains unaltered, the main changes consisting in a thorough revision of the chapters on impedance, supersonics and sound reproduction. Dr. Richardson keeps fully up to date in his knowledge of the literature of his subject, and his book is to be unreservedly commended as a suitable introduction to advanced study and research in a subject which is advancing with remarkable rapidity.

A. F.

**Colloid Chemistry (A Textbook).** By HARRY BOYER WEISER. (New York: John Wiley & Sons, Inc. 1939.) Pp. viii + 428. Price 24s. net.

Professor Weiser has given us in this volume a sound, well-balanced, and very readable introduction to Colloid Science, in moderate compass. It is more descriptive than profoundly theoretical, but the principal theoretical foundations are clearly given, though some of the mathematical proofs fall short of thorough accuracy.

After a brief introductory chapter there are about 100 pages on Surface Chemistry, in which adsorption is treated at length, and wetting and the structure of surface films rather briefly, but with the principal facts and theories indicated well. Some 35 pages deal with the preparation and purification of sols, and an equal space is devoted to some of their physical properties. The electrical properties and the coagulation of sols fill 80 pages; gels, emulsions, foams, smokes and other topics fill another 80 pages. The last part of the book contains a brief account of some important contact catalyses, and of dyeing and clays. References to the literature are well selected and reasonably numerous.

The reviewer would have liked a better treatment of colloidal electrolytes; the few pages on this topic, which has come into great prominence lately on account both of its theoretical interest and of its technical importance, are inadequate. Hydrophilic colloids, though better treated, might receive more attention. No attempt is made, probably wisely, to discuss modern synthetic polymers, or the biological applications. A pleasing feature of the book is, however, the frequent indication of various technical applications.

Few errors have been noticed; on p. 110 the curve for the gaseous film has been displaced upwards so that the limiting value for  $FA/kT$  does not reach unity, as it should do, when  $F$  is zero; and if the reference to "blue sky" in the index is looked up, the reader will find only the unsullied whiteness of the excellent paper on which the book is printed. Misprints seem very few.

Students and non-specialists in colloids will thank the author for providing one of the best descriptive introductions to the subject that has yet appeared.

N. K. A.

**The Raman Effect and its Chemical Applications.** By JAMES H. HIBBEN and EDWARD TELLER. American Chemical Society Monograph Series. The Reinhold Publishing Corporation, New York, 1939. Chapman & Hall, Ltd., London. 66s. net.

Headings to the main divisions of this book will indicate its purpose and scope. These are: Part I—General Discussion on the Raman Effect; its Practice and Theory; Part II, the Raman Spectra of Organic Compounds; and Part III, the Raman Spectra of Inorganic Compounds.

In the first Part, the Effect is described in simple language, with its relationship to absorption and fluorescence; the experimental methods for determining the shift of the lines, their intensities and polarisation are then given; a chapter on the vibration and rotation of polyatomic molecules follows with one on the relationship between infra-red absorption spectra and the Raman Effect; with finally a discussion on the vibrations occurring in different types of molecules and on such features as anharmonicity.

All this theoretical treatment is admirable and presents a clear picture of the information derivable from this study, enabling the observer to calculate the force systems from observed frequencies.

The application of the Raman Effect to constitutional problems is the theme of Parts II and III. Thus in Part II the Raman Spectra of the aliphatic hydrocarbons and their derivatives and of the aromatic hydrocarbons and their derivatives are discussed, together with accounts of the shift characteristic of the ethylenic and the carbonyl linkages. Indications relative to structure are followed up in a multitude of cases.

Part III dealing with inorganic compounds is perhaps necessarily less systematic, but it covers a wide range. Thus the Raman spectra of gases, phosphorus, sulphur, carbon, water, halogen compounds, acids, sulphur and silicon compounds, oxides, azides and ammonium compounds all come under discussion with a wealth of data embodied in the text.

A bibliography extending to about 2000 references, an index of organic and inorganic compounds, linked up with these references, and a numerical index connecting the subjects mentioned in the bibliography and their discussion in the text, show the thoroughness with which this book has been compiled.

It may be truly said that this work is indispensable to workers in this field and in that of the complementary one of infra-red spectra.

R. R.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1939. (The Chemical Society. Pp. 458. Price 13s. Post free.)

Perusal of these volumes impresses one more and more each year with the all-embracing influence of physical chemistry on every aspect of chemical advance. Though H. W. Melville with R. P. Bell, M. G. Evans, W. C. Price and J. H. Schulman have written six excellent monographs under the heading "General and Physical Chemistry," occupying in all 83 pages, members of the Faraday Society will read with equal interest many articles under other general heads, notably those of Peierls on the Theory of Nuclear Forces, of Terrey on Heterogeneous Equilibria, of H. J. Emeléus on Reactions in Non-Aqueous Solutions, of Ubbelohde on Crystal Physics, of Hampson and J. M. Robertson on Inorganic and Organic Structures respectively, and, within the 149 pages devoted to Organic Chemistry, those of H. B. Watson on Reaction Mechanisms and of Maitland on Stereochemistry.

The Annual Reports are useful, not solely for the monographs on subjects with which we feel ourselves somewhat familiar, though it is by such we are apt to judge the value of the whole. Their main interest lies in the opportunity they give us to obtain an adequate perspective view of the less familiar, written by experts.

In these days of stress, when there is little time or opportunity to study the vast field of physical and chemical literature, this volume should be more than usually in demand.

#### ERRATUM.

P. 510. Line 8 from bottom. *For* "thianthren" *read* "phenthiazine."

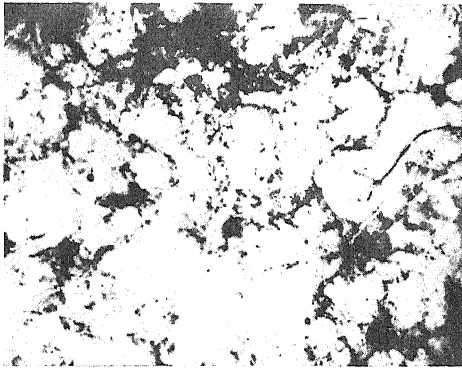


FIG. 1.

[See page 700.



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